OIL WELL CEMENT WITH CARBON NANOTUBE FOR HIGH PRESSURE HIGH TEMPERATURE APPLICATIONS

BY

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This thesis, written by **Waqas Ahmed Khan** under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE in PETROLEUM ENGINEERING**.

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Dedicated to

My Beloved Ami and Abu

&

My Beloved sisters

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In the Name of Allah, the Most Beneficent, the Most Merciful.

"…This is by the Grace of my Lord to test me whether I am grateful or ungrateful! And whoever is grateful, truly, his gratitude is for (the good of) his own self, and whoever is ungrateful, (he is ungrateful only for the loss of his own self). Certainly! My Lord is Rich (Free of all wants), Bountiful."

Surat An-Naml: Verse 40

I begin with the name of Allah, the most beneficent, the most merciful. May Allah bestow peace on our beloved Prophet Mohammed (*peace and blessings of Allah be upon him*), his pure family, his noble companions, and all those who follow them with righteousness until the Day of Judgment. I would never have been able to finish my research without the guidance of Allah who endowed me with health, aptitude and patience.

I would like to pay my deepest respect and gratitude to my beloved parents who have been a constant source of motivation, appreciation and prayers throughout my life. No amount of "thank you" can suffice for the hardships they had to bear to make me a person I am today. I can never thank them enough and can only pray to God to bless them in this dunya and akhirah. If only my words can convey the emotions, I would just like to say I love you both very much and I dedicate my lifelong achievements to you. Special thanks to my sisters for their unconditional support and prayers.

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ABSTRACT (ENGLISH)

NAME: Waqas Ahmed Khan

TITLE: Oil Well Cement with Carbon Nanotube for High Pressure High Temperature Applications

MAJOR FIELD: Petroleum Engineering

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The main purpose of cementing in an oil well is to prevent fluid movement between zones inside the formation and to bond and sustain the casing. Besides these, the cement sheath also shields casing from corroding, guards the casing from shock loads when drilling deeper, and plugs lost circulation or thief zones. As soon as the cement is placed in the wellbore, initial setting occurs wherein development of compressive strength turn out to be more significant for more drilling operations.

There are several applications of Nano particles in different industries such as polymers, electronics, bio-medicines and in concrete industry. Their high surface area and small size, makes them appealing to the petroleum industry. Their use in petroleum industry is making headways in last few years.

In this thesis, we will examine the influence of addition of Carbon Nano Tubes (CNT) on oil well cement at high pressure and high temperature (HPHT). Carbon nanotube will be added at different percentages to the cement slurry mixture presently used for oil/gas well

cementing in Saudi Arabia. Experimental study will address different cement slurry properties such as thickening time, free water separation, rheological properties, compressive strength, density, SEM, XRD and thin section. The most favorable slurry design will be carefully chosen on the basis results of different percentages of CNT used in experiments.

ABSTRACT (ARABIC)

ملخص الرسالة

الاسم: وقاص أحمد خان

عنوان الرسالة: سمنتة أبار النفط بإستخدام الأنابيب النانوية الكربونية لتطبيقات الضغط العالي ودرجة الحرارة العالية

التخصص: الهندسة البترول

تأريخ التخرج: مايو 2015م

إن الغرض الأساسي من عملية سمنتة أبار النفط هو منع حركة الموائع بين الطبقات داخل التكوين الصخري للأرض وأيضاً لربط وتسنيد البطانة. بجانب ذلك، الغلاف الإسمنتي يحمي البطانة من التآكل، ويحافظ على البطانة من الصدمات أثناء الحفر بأعماق بعيدة، ويسد الطبقات الضعيفة ذات المسامية العالية من فقدان دورة السائل داخل التكوين الصخري. طالما أن الإسمنت وضع داخل باطن البئر، تحدث عملية الإعداد الأوّلي بحيث أن عملية تحسين القوة الإنضغاطية للإسمنت تصبح أكثر أهمية لعمليات الحفر.

تستخدم تقنية النانو في العديد من التطبيقات وفي مختلف الصناعات كصناعة البوليمرات والإلكترونيات والأدوية الحيوية وصناعة الخرسانات. تمتاز أجزاء النانو بأنها ذات مساحة سطح عالية وحجم صغير، هذه الميزات جعلتها محبذة الإستخدام في صناعة النفط. أحرزت إستخدام تقنية النانو في صناعة النفط تقدماً في السنوات الأخيرة.

في هذه الرسالة، سندرس تأثير إضافة الأنابيب النانوية الكربونية (CNT) في إسمنت أبار النفط تحت ظروف الضغط ودرجة الحرارة العالتين (HPHT). هذه الأنابيب النانوية الكربونية ستضاف بنسب مختلفة لخليط الإسمنت المستخدم حالياً في عملية سمنتة الأبار في المملكة العربية السعودية. ستجرى دراسات مخبرية لمعرفة خصائص خليط الإسمنت كزمن التثخين، خاصية فصل الماء الحر، الخواص الريولوجية (الخواص المتعلقة بتشوه المادة)، القوة

الإنضغاطية، الكثافة، دراسة المجهر الإلكتروني الماسح (SEM)، دراسة البلورات بالأشعة السينية (XRD) ودراسة الرقائق. سيتم اختيار أفضل تصميم لخليط الإسمنت وفقاً للنتائج الأساسية التي يتم الحصول عليها من التجارب بإستخدام نسب مختلفة من الأنابيب النانوية الكربونية (CNT).

CHAPTER 1

INTRODUCTION

1.1 OVERVIEW

Oil and gas production and its exploration have an ultimate influence on the world's economic structure. As the easily reachable petroleum resources have been developed and produced during the last decades, extra exploratory pursuit and development of oil fields in severe environment as well as unconventional oil reserves are essential in order to meet the worlds growing energy demand. Over the last two decades, the amount of oil consumption per year has exceeded the amount of newly found oil reserves. Therefore, with time, the prospect of an ultimate decline in oil production is becoming a realistic scenario. Though, the precise quantity of undiscovered oil reserves is not well known. The search for new oil and gas reserves is getting extreme in terms of depth, temperature and pressure. In deeper wells, high pressure and high temperature and post cementing operations put great stresses on the cement sheath which could affect the reliability of the cement. Need of systematic studies on existing cementing techniques and developing new

technology is an important part in order to avoid health, safety and environmental (HSE) issues. The design of cement slurry is very precarious and it must possess properties which guarantee the stability and long term integrity of cement sheath under high pressure high temperature (HPHT) conditions.

Inappropriate well design and well cementing can put at risk the oil production from the well and have high economic impact. Oil spills such as the latest Gulf of Mexico deep water horizon oil spill are some of the reasons of oil loss from the global reserve. These types of incidents not only cause economic losses but also cause environmental disasters particularly in marine habitats because of toxic substances. Manufacturing justifiable oil wells is a foremost worry for countries with vast oil production like Saudi Arabia (KSA). The KSA has 267 billion barrels of confirmed oil reserves with 100 major oil and gas fields comprising of over 1500 active oil wells. Most of these reserves are comparatively deep and sustain elevated temperatures and pressure. The KSA also has the fourth largest global gas reserves of 253 trillion cubic feet. In 2008, crude oil production capability in Saudi Arabia was approximately 11 million barrels/day, and was projected to increase to around 12.5 million barrels/day by the year 2009. Throughout 2008, 87 wells were drilled and Saudi Aramco intended to invest $60 billion in oil and gas projects over the next five years. Several other countries are also beginning to invest in and produce unprecedented amounts of oil output, as seen domestically with production at the highest levels in 15 years.

Well cementing is one of the key processes performed during drilling and completion of wells and has a significant effect on the life of the well but it depends on the area drilled and segments encountered. Oil well cement slurry is incorporated during well drilling operations to assist in the drilling procedure. Therefore exceptional consideration has to be given to cement practices particularly in high pressure and high temperature (HPHT) wells. Zonal separation can be successfully achieved if the cement has good bonding properties with casing and the formation. The bonding properties can be disturbed by cement shrinkage and pressure fluctuations made by downhole deviation of pressure and temperature. The wells are exposed to high temperature changes in HPHT formations and these variations distress both the formation and the casings, triggering expansion and contraction. Due to these expansions and contractions of casing and plastic formation like salt results in cracks in the already set cement.

Cement sets after undergoing hydration reaction. Hydration reaction occurs when water and cement reaction takes place. Ideally, the cement mixture is developed to provide low permeability matrix and thereby isolate the well during drilling, production and further until the well is abandoned. Unfortunately this is not always the case, due to several influencing factors and downhole conditions. The annular cement sheath may fail throughout the life time of the well and thereby cause loss of well integrity. Inadequate zonal cementing can lead to unnecessary loss of reservoir (pumping) pressure, loss of hydrocarbons and in worst case losing the well due to casing collapse, thus affecting the

financial viability of the project. In addition, hydrocarbons flow behind the casing may also affect water aquifers on the way to surface, causing environmental disasters (Abbas et al., Nelson and Guillot, 2006).

If the hydration process is constant, the decrease in the pore space of the setting cement results in the reduction of its pore pressure. The post-set cement consisting of minimal number of pore spaces when subjected to high loads in deep wells compression sets in and destroys the cement sheath by compaction of matrix porosity. Mechanical failure or damage in the well can cause destruction of cement matrix and can result in the creation of cracks in the cement matrix. Gas migration from the formation to the surface can occur through these cracks, thus reducing the life of the well. (Yetunde & Ogbonna, 2011).

Migration of gas through cement has been a major issue in oil industry for several years. According to a study, approximately 80% of wells in Gulf of Mexico have gas migration problem through cemented casing. The hydration process continues and consequently development of the strength, after the cement has set, for twelve months or more. After this time, it retains the strength that it has achieved but if it is attacked by means of erosion. Cement will reach supreme strength after 15 days once exposed to temperatures beyond 230 °F.

The already set cement slowly starts to lose its strength, after the first two weeks. This phenomenon of the set cement losing its strength is called strength retrogression. Cement degradation can occur due to changes in structure and water loss. The set cement contains a complex CSH. This calcium silicate hydrate is transformed to a feeble porous structure (alpha-di calcium silicate) which results in strength retrogression, at temperatures around

250 °F. The rate of occurrence of these changes depends on temperature (Joel & Iseghohi, 2009).

The proper cement slurry design for well cementing is function of many factors, comprising the well bore geometry, casing hardware, formation integrity, drilling mud characteristics, existence of spacers and washers, and mixing conditions. The properties of cement has been enhanced, in the past few decades, by presenting numerous forms of novel chemical admixtures such as retarders, viscosity modifiers, accelerators, strength developing admixtures etc. The type and dosage of chemical admixtures being used in the cement determines the early age and hardened properties of cement systems. The chemical and physical properties of the cement strongly influence the performance of chemical admixtures. The interactions of OWC with different types of admixtures and the associated cement-admixture compatibility at high temperature are still largely unexplored.

To the extent of our knowledge, though, so far, no literature describing real usage of Nanomaterials with other additives to improve properties of cement slurry systems for oilfield application has been documented. The objective of this study is to demonstrate Nano materials help to enhance the properties of cement. The core emphasis of research is on the effect of Carbon Nano Tube (CNT) material on the cement performance in high pressure/temperature environment. A well located in the Middle East is selected to study the cement mixture design and then CNT material is added and the several effects are determined to select the optimum cement slurry design.

1.2 CARBON NANOTUBES

Carbon nanotubes (CNTs) have always existed in nature; however, they were first discovered by Russian scientists; L. V. Radushkevich and V. M. Lukyanovich, in 1952, where clear images of the CNTs were published in a journal paper (in Russian language). However, CNTs have not been scientifically recognized and used until the last two decades. In 1991 Sumio Iijima [15], published the first article that systematically describes the formation of a helical microtubes made of pure carbon atoms linked together by carbon-carbon (C-C) bonds.

There are many known forms for carbon structures in nature, like diamond, graphite, graphene and fullerenes (Buckyballs). CNTs can be imagined as a rolled graphene sheet which its structure is made of a one layer of carbon atoms bonded by a carbon sp2 bonds in hexagonal pattern. Graphene sheets were investigated by man for the first time in year 2004, by the Russian scientists Nobel Prize winners in physics (2010) Andre Geim and Konstantin Novoselov, from University of Manchester, UK. CNTs can be assumed to be a graphene sheet then rolled in a cylindrical (tube) shape and closed at the two ends by half fullerenes or another carbon structure.

These rolled tubes can be formed as a single tube with one cylinder and is called single walled carbon nanotube (SWCNT), or it may be made from multiple layers of the carbon nanotube, as if they are many cylinders inside each other (from 2 to 20 concentric layers), and called multi walled carbon nanotubes (MWCNTs). The size of the CNTs is in nano scale, the diameter could vary from 1 to 4 nanometers for SWCNTs, and 5 to 50

nanometers or more for the MWCNTs, where the length can extend into several micrometers.

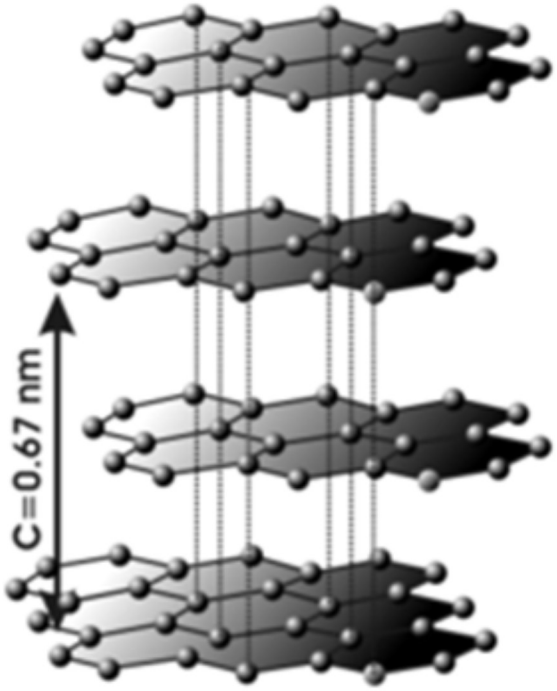

Figure 1.1 Graphite Structure

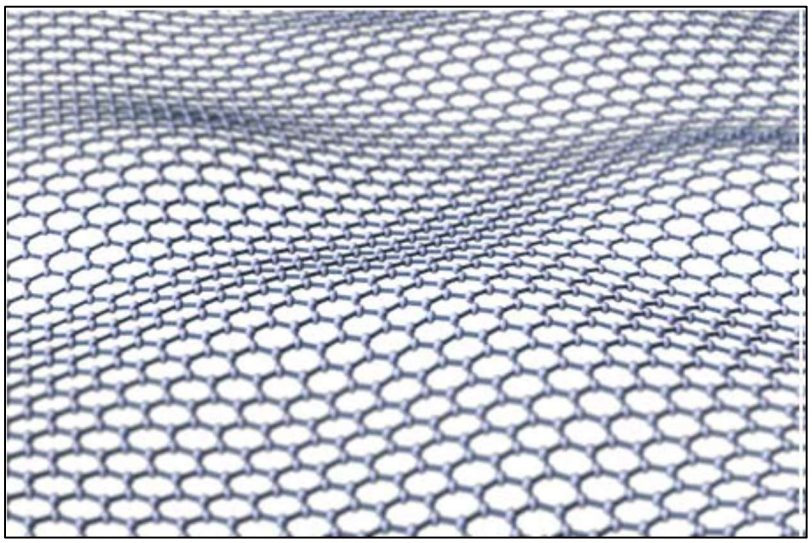

Figure 1.2 Graphene Sheet

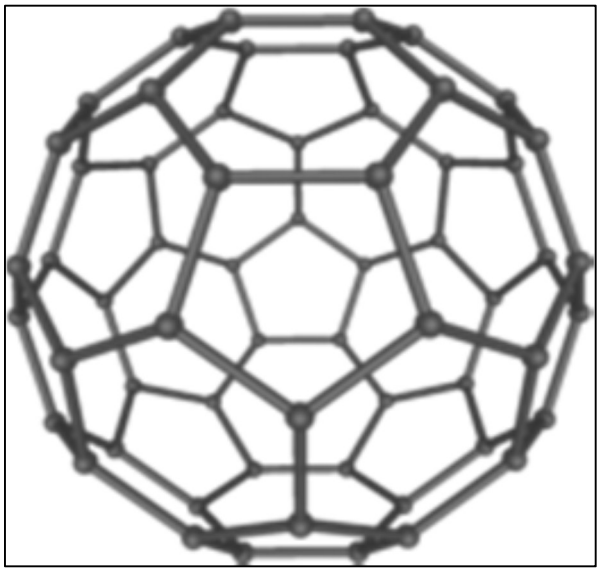

Figure 1.3 Fullerenes (BuckyBall) Structure

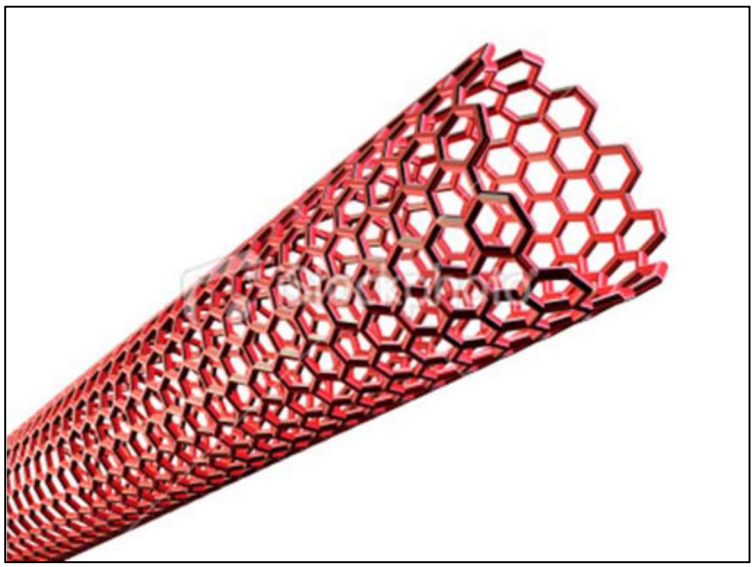

Figure 1.4 Schematic of a Single Walled Carbon Nanotube (SWCNT), comprised of single layer of Carbon Nanotube.

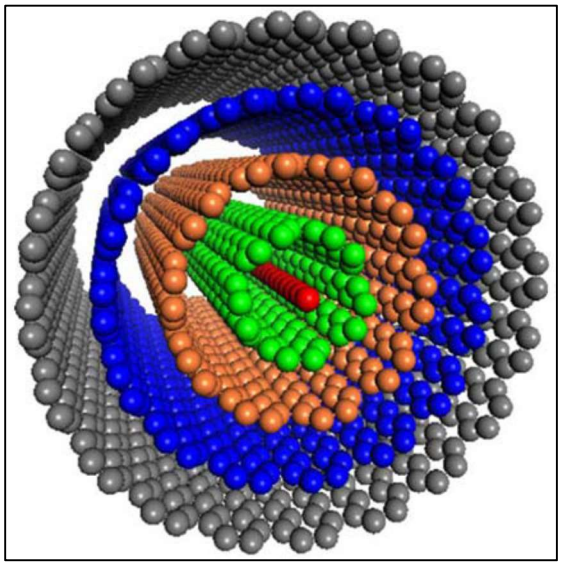

Figure 1.5 Schematic of a Multi-Walled Carbon Nanotube (MWCNT), comprised of many concentric layers of Carbon Nanotubes

1.3 NEED FOR THIS RESEARCH

The petroleum industry encounters several challenges in different areas and need more researches to yield in improvements and developments. One of the most difficult challenges associated with drilling and completion operations is assuring good cementing job in high temperature and pressure wells. Poor cementing jobs could result in serious consequences that may jeopardize the success of any oil and gas well. Communications between zones, gas migration, undesired fluids entry, strength retrogression and stresses are examples of the serious consequences resulting from poor cementing jobs in HPHT wells. Companies and the academia are continuously conducting research projects to improve and develop new cements and chemical additives that enhance cementing oil and gas wells in hostile environments.

Because of high costs and greater risk of adapting new technologies, the application in oil and gas industry has not been fully discovered. However, the quest for efficiency in the current economic situation has been the driving force behind development of new technologies. Nanotechnology itself is not a new field, but its use in the oil and gas industry is certainly in its infancy, including drilling applications.

1.4 PROBLEM STATEMENT

The application of nanotechnology to oil and gas industry is rapidly becoming an important area for research and development and this research aims to provide the benefits of nanomaterial for oil cement systems. Few literature reports are available mentioning use of Nano-materials in the petroleum industry.

Since cement slurry is pumped into the wellbore; issues such as thickening time, rheology, water loss, gas migration, development of slurry strength with time and cement shrinkage are as critical as high compressive strength developed after set. The research will investigate the effects of Carbon Nanotubes on oil well cement slurry using Type-G cement which is used in oil and gas well cementing in Saudi Arabia.

1.5 THESIS OBJECTIVES

In this research, experiments were conducted in order to examine the significance of Carbon nano tube incorporation in Type G Oil well cement (OWC) pastes. Type G OWC was used in this study because it is a common cementing material capable of being implemented from the surface of the oil well bore head all the way down to a depth of approximately 20,000 ft, over a wide range of temperatures and pressures. Investigation of this type of cement becomes important as hydrocarbon exploration reaches greater and greater depths.

The present study attempts to develop a better understanding of the important mechanisms that controls the properties of OWC slurry subjected to severe conditions such as high temperature and pressure, and to investigate the performance of Carbon Nanotube admixture in controlling the properties of oil well cement slurries. This knowledge thus gained could ultimately allow the optimization of blended oil well cements, leading both to ecological and economic benefits.

The following properties of OWC slurry using CNT will be studied:

a) Thickening Time
b) Free water separation
c) Rheological Properties
d) Compressive Strength
e) Density
f) Porosity and permeability tests
g) XRD and SEM analysis

1.6 THESIS ORGANIZATION

This thesis has been prepared according to the guidelines stated by the Deanship of Graduate Studies of King Fahd University of Petroleum & Mineral. It has been divided into five chapters as follows;

Chapter 2: explains the literature review which covers the basics of cement, factors affecting cement design, additives and different cement properties. It discusses the previous researches conducted on the cement slurry development and different additives improvement over the years.

Chapter 3: explains the experimental program used for this research work. It presents the complete methodology of tests according to API Specifications conducted to measure the different properties of cement in high pressure and temperature conditions.

Chapter 4: presents the results and discussions of all experimental tests conducted to analyze the behavior of cement.

Chapter 5: concludes and highlights the major research outcomes with recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Oil well cementing is the process of placing cement slurry in the annulus space between the well casing and the geological formations surrounding to the well bore. When a certain section of the depth of an oil or gas well has been drilled successfully, the drilling fluid cannot permanently prevent the well bore from collapsing. Therefore, oil well cementing was introduced in the late 1920s (Joshi and Lohita, 1997) with a number of objectives: (i) protecting oil producing zones from salt water flow, (ii) protecting the well casing from collapse under pressure, (iii) protecting well casings from corrosion, (iv) reducing the risk of ground water contamination by oil, gas or salt water, (v) bonding and supporting the casing (Labibzadeh, Zahabizadeh, & Khajehdezfuly, 2010), and (vi) providing zonal isolation of different subterranean formations in order to prevent exchange of gas or fluids among different geological formations (Jones, Carpenter & Co, 1991).

In addition to their exposure to hostile temperature and pressure conditions, oil well cements (OWCs) are often designed to cope with weak or porous formations, corrosive fluids, and over pressured formations. The appropriate cement slurry design for well cementing is a function of various parameters, including the well bore geometry, casing hardware, formation integrity, drilling mud characteristics, presence of spacers and washers, and mixing conditions. The behavior of OWC slurries must be optimized to achieve effective well cementing operation. A strict control of the hardened cement mechanical properties and durability during the service life of the well are very important criteria, especially under such severe environments. Thus, a special class of cements called oil well cements (OWCs), has emerged and is specified by the American Petroleum Institute (API) (API Specification-10A, 2012). A number of additives have also been used to alter the chemical and physical properties of the OWC slurries as required for the flow ability, stability of the slurry and to ensure long term performance of wells.

Extensive research has been conducted to improve the efficiency of oil well production by improving the physical and mechanical properties of OWC slurries. This chapter discusses the basic concepts involved in oil well cementing, the different types of OWCs, and their chemical and physical properties. An insight into the additives that can modify the behavior of the OWC systems and allow successful slurry placement between the casing and the formation, rapid compressive strength development, and adequate zonal isolation during the lifetime of the well is also provided.

2.2 WELL CEMENT

A typical oil/gas well can be several thousand meters in depth, and of a few inches in diameter (Lafarge, 2009), and is usually constructed using a metal casing surrounded by a special cement slurry mix that seals the annulus space between the outer face of the tubing and the wall formation of the hole. Cement slurries are sometimes pumped to depths in excess of 6000 m (20000 ft). At these depths, hydrated Portland cement are subjected to temperatures in excess of 230◦F, so it undergoes significant phase changes which result in substantial decrease in compressive strength of the cement slurry and increases its permeability at temperatures above 230◦F as a result of strength retrogression arising from the breakdown of its crystalline structure at such temperatures (Mehta and Monteiro, 2001). This would render the Portland cement ineffectual for high temperature applications.

After drilling the well to the desired depth, the drill pipe is removed and a longer string of casing is run into the well until it reaches its bottom. The circulatable completion fluids such as drilling mud must be removed and replaced with a hardened cement to ensure intimate contact and bonding of the cement with the casing and formation surfaces. Sufficient cement slurry is pumped down the inside of the casing and forced up the outside of the casing through the annular space between the casing and subterranean borehole wall (Detroit, 1983) using two-plug cementing method (Calvert, 2006; Oilfield Glossary, 2009).

Pressure is applied above plugs by an aqueous displacement fluid to displace remaining cement slurry (Detroit et al., 1983). Two types of cementing plug (top and bottom) are typically used on a cementing operation to allow the cement slurry to pass through the casing and to reduce the contamination of cement slurries by other fluids that remain inside the casing prior to pumping cement slurry (Oilfield Glossary, 2009).

Typically, the cement slurry is brought much higher than the production zones into the well bore to exclude undesirable fluids from the well bore so as to protect fresh water zones and corrosion of the casing (Calvert, 2006). After the cementing process, a curing time is allowed for the slurry to harden before beginning completion work or drilling to a deeper horizon. The set cement slurry forms a low permeability annulus and isolates the productive zone of the well from the rest of the formation.

2.3 CLASSIFICATION OF OIL WELL CEMENT

Oilwell cements are usually made from Portland cement clinker or from blended hydraulic cements. OWCs provide a base constituent in the slurry mix that is pumped into the interior metal casing of the well and forced back toward the surface from the base of the borehole filling the annulus (Powers et al., 1977, Detroit et al., 1981, Calvert, 2006). In the start, merely one or two kinds of oil well cement were existing. The more tough performance standards could not be fulfilled by those kinds of cements, as oil/gas wells became deeper and exposed to more hostile environments. Improved OWCs were developed with the advent of the API Standardization Committee in 1937. (Smith, 1987)

The API Specifications for Materials and Testing for Well Cements (API Specification 10A, 2002) comprise requirements for eight classes of OWCs (classes A through H) as explained in **Table** 2.1. OWCs are categorized into grades based upon their C_3A (Tricalcium Aluminate) content: Ordinary (O), Moderate Sulphate Resistant (MSR), and High Sulphate Resistant (HSR). There is a certain range of well depth, temperature, pressure and sulphate environments which is applicable for each class.

The three most generally used oil well cements are Class A, Class G and Class H. For milder and less demanding well conditions, Class A is used. For deeper, hotter and higher pressure well conditions, Class G and H cements are usually specified. (Lafarge, 2009) Conventional types of Portland cement incorporating suitable additives have also been used. The chemical composition of cement is what distinguishes one type of oil well cement from another and determines the suitability of the cement for specific uses. The chemical composition of OWC is slightly different from that of regular Portland cement. OWCs usually have lower C3A contents, are coarsely ground, may contain friction reducing additives and special retarders such as starch, sugars, etc, in addition to or in place of gypsum (Popovics, 1992). The key features of commonly used OWCs are summarized in **Table** 2.1.

The most commonly used OWCs today are API Class G and Class H. These two cement types have similar chemical composition but have difference in their surface area. Class H is coarser than Class G cement and thus has a lower water requirement. Cement that is ground too fine should not be used as oil well cement.

Development of sufficient compressive strength to hold the casing in downhole condition cannot be achieved if microfine cements and ultra-fine (blain surface> 9000 cm_2/gm) portland cements are used for primary cementing. It also does not generally have adequate sulphate resistance. In case of repairing the oil well, micro fine cement is a good option because typical oil well cements cannot be used because of their higher particle size and the subsequent difficulty to penetrate in extremely small cracks/channels (Kumar et al., 2002).

Table 2.1: Key features of API Oil Well Cement (API Specification 10A, 2002)

Cement Class	**A**	**B**	**C**	**D**	**E**	**F**	**G**	**H**
W/C, % mass fraction of cement	46	46	56	38	38	38	44	38
Range of depth (ft)	0 to 6000	0 to 6000	0 to 6000	6000 to 10,000	10,000 to 14,000	10,000 to 16,000	0 to 8,000	0 to 8,000
Availability	In Ordinary type, similar to ASTM Type I	MSR & HSR grades, similar to ASTM Type II	In all 3 degrees of sulfate resistance, similar to ASTM Type III	MSR & HSR grades	MSR & HSR grades	MSR & HSR grades	MSR & HSR grades	MSR & HSR grades
Cost	Lower Cost	Lower Cost	Lower Cost	More costly than OPC	More costly than OPC	More costly than OPC	-	-

On the other hand, American Society for Testing and Materials (ASTM) Specification C-150 develops eight types of Portland cement I-VIII with type I cement being the normal, general-purpose cement used for construction purposes. More than 92% of Portland cement used in the United States are type I and II (or Type I/II). **Table** 2.2 shows the ASTM cement classification and their use.

Table 2.2: ASTM cement Classification

ASTM Cement Class	Use
I	General purpose cement, when there are no extenuating conditions. Similar to API class A.
II	Aids in providing moderate resistance to sulfate attack. Similar to API class B
III	When a high early strength is required. Similar to API class C
IV	When a low heat of hydration is desired
V	When high sulfate resistance is required
IA	A type I cement containing an integral air- entraining agent
IIA	A type II cement containing an integral air- entraining agent
IIIA	A type III cement containing an integral air- entraining agent

2.4 OIL WELL CEMENT ADDITIVES

Typical admixtures for OWC slurries can be categorized into eight groups: accelerators, retarders, extenders, weighting agents, dispersants, fluid-loss control agents, lost circulation control agents, and other special additives (antifoam agents, fibers, etc.). The OWC slurry may incorporate retarders or accelerators to control the setting behavior, weighting agents are light-weight systems to increase the density of the OWC slurry system, and extenders to lower the density of the cement system and increase its yield. Similarly, different admixtures are used as dispersants or viscosifiers to control the viscosity of the slurry. For instance, fluid loss additives are used to control the loss of the aqueous phase of the OWC slurry to the geological formation and to maintain constant water to solid ratio in cement slurries, while lost circulation control agents are used to control the loss of the cement slurry to weak or regular formations. A detailed review of cement additives has been provided by Nelson et al. (1990 and 2006). Other than chemical admixtures, several mineral additives such as fly ash, silica (α-quartz and condensed silica fume), diatomaceous earth, gilsonite, powdered coal (Nelson et al. 1990; Nelson et al., 2006), etc., have been used to modify certain properties of OWC slurries.

2.4.1 Accelerators

This additive is used to reduce slurry's set time and let the slurry to acquire required early compressive strength in a practical time frame (Santra et al., 2012). These additives are used for shallow wells having low temperature and pressure conditions for cement jobs

where long thickening time is not necessary. Calcium chloride, sodium chloride and gypsum are the most commonly used accelerators.

2.4.2 Retarders

This additive is used to delay slurry's set time. Due to this delay, hardening of the cement occurs after the cement has been placed. The effect of increased temperature on cement slurry is countered by this type of additives. Calcium lignosulfate and borax are the most commonly used retarders.

2.4.3 Fluid Loss Agent

This type of additive is used to prevent cement from hardening incorrectly due to excessive losses of water to the formation. These additives are used to decrease excessive losses of water to the formation.

In addition, these additives:

- Increase viscosity
- Delay the set time
- Control free water in the slurry

The organic polymers and cellulose derivatives are the most common fluid loss agents used.

2.4.4 Extenders

This additive is used for cementing across weak formations by reducing the density of the slurry. Lower density slurry lowers the hydrostatic pressure and helps prevent formation damage. Fly ash and sodium silicate are the mostly used extenders.

2.4.5 Anti-foaming Agents

One of the problems associated with cement slurry while mixing is cement foaming. Damage to the pumps in the field can be caused if the air is entrapped in the cement slurry. Cement foaming can result in inappropriate density readings and so mixing incorrect cement slurry density.

This additive is used to reduce foaming problems and is normally used in all cement design. These are exceptional additives which are developed by different companies and are accessible in powder or liquid for suitable use.

2.4.6 Free Water Control Additives

These additives tie up water in light weight or extended slurries. The slurry properties changes as the water is absorbed into the surrounding formations so it is important to control this water loss. Slurry flow and placement is affected by this absorption. Commonly used free water additive is Aluminum chlorohydrate.

2.4.7 Lost Circulation Control Agents

Lost circulation can occur when cementing against very permeable and vuggy formations as well as formations having natural or induced fractures. It is an important issue to be considered.

Reducing cement slurry density and by adding additives to act as a plugging bridge on the opening area of the high permeability zone or the fracture can help in controlling Lost circulation. Granular type (e.g. Gilsonite), flake type (e.g. cellophane), and fibrous agents (e.g. nylon) are the different types of lost circulation control agents being used.

2.4.8 Weighing Agent

These additives can be used to increase the density of the cement or slag which also helps in controlling formation pressures. Mostly used weighing materials are barite and hematite.

2.4.9 Dispersants

Dispersants (also known as Super Plasticizer / Friction reducer) decrease slurry viscosity, which is crucial for placement and cohesion of cement slurries. Appropriate dispersion of a slurry results in:

- Improved early compressive strength
- Better fluid-loss control
- Better free-water control

Commonly used dispersants are naphthalene sulfonate and broxin.

2.4.10 Strength Retrogression Agents

Compressive strength of cement slurries starts to decrease over time when they remain at temperatures above 200°F (94°C). This phenomenon is called strength retrogression and it can be decreased or prevented by adding alternative source of silica, such as silica flour or silica sand, to the slurry (Iverson et al., 2010).

2.5 NANO MATERIALS

The oil products global demand is predicted to be increased by 50% in the next 20 years. However, the use of unconventional energy sources, such as nuclear and renewable energy will increase in the coming years, this increase will be comparatively small and the main role of the these unconventional energy sources will be to balance and complement, rather to swap the use of hydrocarbons. Therefore, meeting the World's growing energy demand will be a major challenge in the coming decades. Nanotechnology has the potential to fill the gap by providing technologies that are more proficient and environment friendly.

Nanotechnology refers to a field of applied science and technology which deals with the control of matter on the atomic and molecular scale, generally 100 nanometers or smaller, and the manufacturing of devices with critical dimensions that lie within that size range (Singh & Ahmed, 2010). Specifically, advancements in nanotechnology have led to development of significantly enhanced enabling materials, tools, and devices with features and characteristics that cannot be matched by conventional technologies.

Nanoparticles provide exceptional properties because of their small size and high surface area per unit volume (see **Figure** 2.1). As a result, they have many useful applications including oil and gas exploration and production. The ability to measure and manipulate matter on the nanometer scale is making possible a new generation of materials with enhanced mechanical, optical, transport and magnetic properties. However, still much remains unknown about nanoparticles and why materials made from nanoparticles differ from those made using their larger counterparts. Nano materials act to be stronger and more reactive than non-Nano materials. It is also unclear why Nano fluids conduct heat so effectively. There is a common assumption that it may be related to the increased surface interface. Since, for a given volume of material, there are a greater number of particles as their size decreases, perhaps there is more surface area for the nanoparticles to conduct the heat. The transition from micro- to nanoparticles leads to changes in physical as well as chemical properties of a material. Two of the major factors are the increase in the ratio of the surface area to volume, and the size of the particle. High surface area-to-volume ratio, which increases as the particles get smaller, leads to an increasing dominance of the behavior of atoms on the surface area of particle over those in the interior of the particle (i.e., surface forces tend to dominate body forces); this affects the properties of the particles when they interact with other particles. As a result of the higher surface area of the nanoparticles, the interaction with other particles within the mixture is greater, potentially leading to increased strength of the material, heat resistance and other properties of the mixture. Nano materials properties depend highly on the shape, orientation and structure of nanoparticles.

Now a day, many Nano materials are being investigated in oil well cementing for example Nano silica, Nano alumina, Carbon Nano tubes and Nano clay. Both Carbon Nano tubes and Nano clay have limited applications in oil well cementing. Our research encircles the effects of Carbon Nanotubes on oil well cementing in HPHT applications.

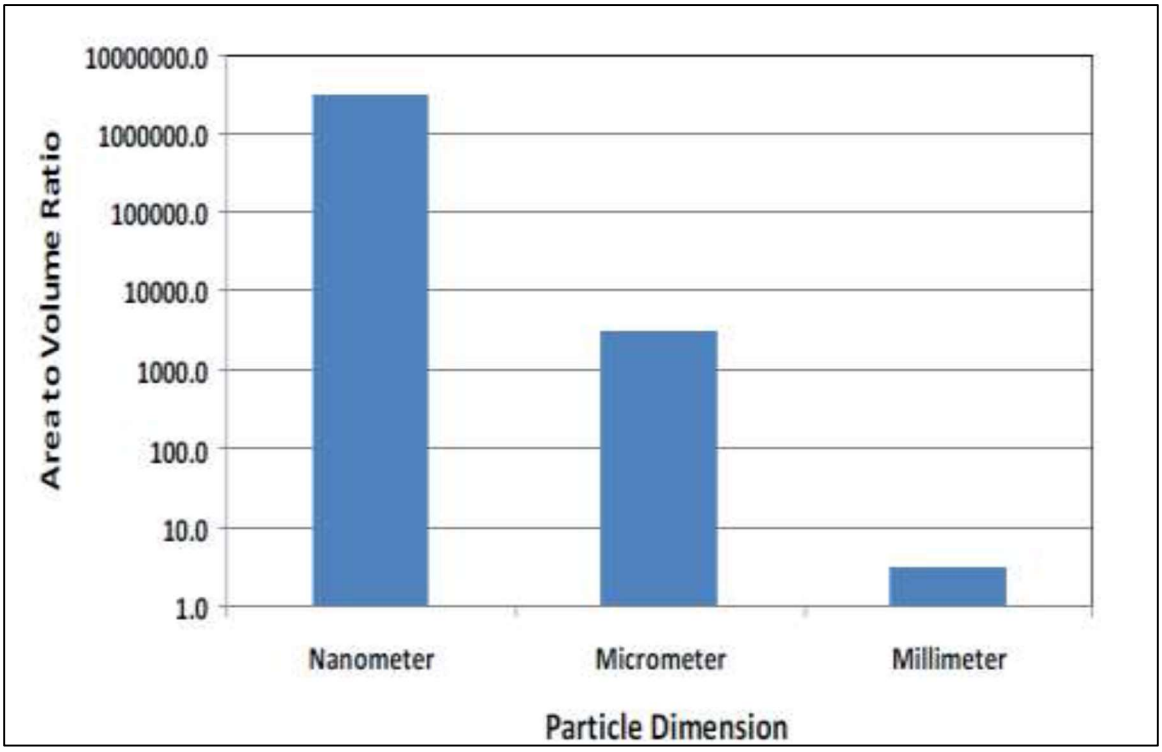

Figure 2.1: Area to volume ratio of different particles dimensions (Saidin, Sonny & Nuruddin, 2008)

2.6 CEMENTING DESIGN PROCESS

The drilling and completion of a well is a capital project that goes into millions of dollars and hence, it is necessary to have inclusive design of the cement used for completion of a

particular well to avoid remedial cement work which would put extra cost to the project. Cement design is usually formulated to a particular well according to prevailing downhole conditions which is followed by testing in the lab to determine if the design would be satisfactory. Ravi and Xenakis, (2007) discussed a three step approach to cement design (see **Figure** 2.2). Step one includes a detailed engineering analysis. It requires classifying the nature of the formation- is it a hard or a loose formation? It requires ascertaining all forces that would come into play as the well is being produced- are there high temperatures, high pressures or both? Is it normally or abnormally pressured? Step one also covers stress analysis to determine if the cement sheath would sustain the series of cyclic loads it would encounter during its lifetime. The answers to step one questions can lead to step two which involves designing the cement slurry based on factors identified in step one. The properties of the cement like tensile strength, Young's modulus, Poisson's ratio, plasticity parameters, shrinkage/expansion during hydration, and post-cement slurry hydration are chosen so as to effectively match the effects of downhole conditions. Thereafter, laboratory investigations are conducted on the designed slurry.

The data from the laboratory tests and the analysis of step one are then analyzed together to evaluate performance. Step three involves best drilling and cementing practices such as centering of casing and effectively cleaning out hole of all mud so as not to undermine the performance of the designed slurry. It also comprises monitoring during the life of the well.

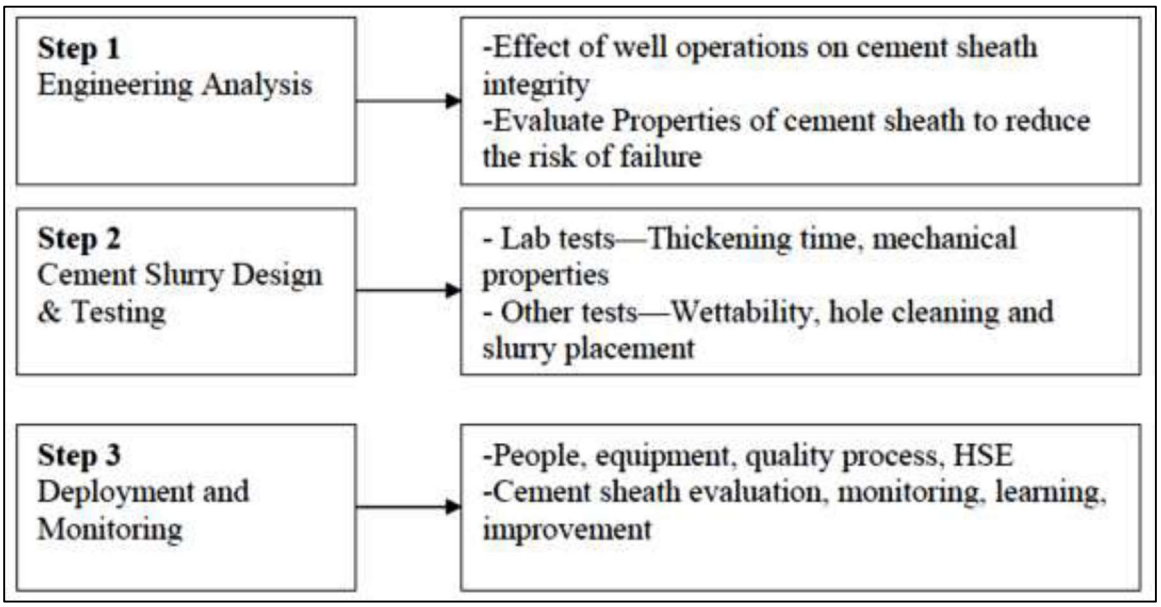

Figure 2.2: Three step process for cement design (Ravi and Xenakis, 2007)

2.7 LITERATURE REVIEW

Parker et al.[1] (1965) presented an efficient technique of replacing the mud from the wellbore while placing cement into the wellbore. Cement when contacted with mud reacts instantly and creates a mass of very high gel strength having properties different from cement and mud. This is a major factor in the success of cementing job. Field results and laboratory studies suggested that low pumping rates for cement helps in effective displacement of mud through the wellbore.

Shell and Laboratorium[2] (1983) presented a theoretical model which explains how a cement slurry loses its hydrostatic head and allows gas influx to occur in the cement sheath. Mud displacement by cement plays an important role in the success of cementing job. A good understanding of efficient cement slurry formulation is required. Some recommendations were given for achievement of successful zonal isolation.

Parcevaux and Sault[3] (1984) investigated the cement bonding properties under controlled temperature and pressure curing conditions. Cement bonding properties were directly proportional to cement shrinkage and elasticity. Laboratory and field experiments were conducted to compare the bonding performance of the standard cement compositions with that of cement composition modified with bonding agent.

Sabins et al.[4] (1984) investigated the effect of excessive retardation on the physical properties of cement slurries. Laboratory studies were conducted to correlate thickening time, retardation to gel strength development, initial set and early compressive strength. Main purpose of thickening time design is to provide ample time to place the slurry in the wellbore. The study concluded that cement slurries must have thickening time of more than 11 hours before over-retardation significantly lengthens the cement transition time.

Sabins and Sutton[5] (1986) further expanded the above study to include a wider range of well conditions. Various slurry types were studied and thorough evaluation of static gel-strength was made. The data generated showed that development of gel strength was more related to the type of slurry than to the thickening time. UCA proved to be an effective instrument of calculating continuous values of compressive strength of cement.

Sauer[6] (1987) presented a comprehensive review of the past and present work on mud displacement during cementing. All the topics related to cementing jobs such as centralization, pipe movement, pipe-lowering speed, hole geometry, job monitoring and the application of each process to the mud displacement process is discussed.

Baret[7] (1988) presented a study on two types of fluid loss behavior during cementing i.e dynamic and static fluid loss. He concluded that the fluid loss in dynamic behavior is dependent on the upper density limit. He also presented formulations for calculating acceptable limits of fluid volume lost and mud cake build up during the respective behaviors. All the problems encountered due to the fluid loss during cementing were also discussed in his study.

Jones et al.[8] (1991) presented a combined (latex and thixotropic) cementing system that improves cement bonding and zonal isolation in wells having bottom hole static temperature below 175 °F. Laboratory studies and case histories indicated that adopting this system will yield in better primary and remedial cementing through gas migration prevention, high degree of zonal isolation, filtrate loss reduction with rapid compressive strength gain, and minimal waiting on cement.

Ruoff and Lorents[9] (1995) estimated the tensile and bending stiffness constants of MWCNT's and SWCNT's in terms of the known elastic properties of graphite. They considered defect free nanotubes for their study. They also studied about the thermal expansion of the nanotubes and concluded that thermal conductivity is highly anisotropic and has the highest value compared to other materials.

Salvetat et al.[10] (1999) conducted an experiment to study about the elastic properties of CNT. He concluded from his study that CNT is known to be the strongest material to be discovered. Researches and experiments have reported that they have moduli of elasticity that exceed 1 TPa in value. HRTEM & AFM techniques were applied to measure the Young's Moduli of SWNT and MWNT.

K.R. Backe, O.B. Lile et al.[11] (1999) studied about the transition period of curing oil well cements. Cement setting process was studied extensively. Different mechanisms were studied which takes place during cement hydration. A new mechanism for gas migration in the cement was proposed which states that gas has to overcome the entry pressure of cement pores. Temperature effect was also studied on the cement hydration chemistry. They also concluded that low shrinkage will mitigate the problem of gas migration.

Yu et al.[12] (2000) estimated the tensile strength for the set of 19 multi-walled carbon nanotubes which was reported to be 63 GPa. Stress-strain curve analysis of the individual MWCNT's was also done. Experiment was carried out to calculate the tensile strength of MWCNT's. TEM examination was carried out on the broken nanotubes which revealed different types of structures.

Hodne et al.[13] (2001) conducted an experiment to study the effect of high temperature on the cement slurry. The cement slurry was prepared in accordance with the API standards. Two types of tests were conducted. One containing only class G cement and in the other cement is partly replaced by silica flour. Various additives were used to

maintain the rheological properties. The rheological properties of the high temperature slurries using various additives were measured.

Heinold et al.[14] (2002) studied the effect of key cement additives on the mechanical properties of normal density cement. Organic and non-organic material were added to oil field cements with water to cement ratio of (0.5-0.66) and then the cements were subjected to unconfined compressive strength tests as well as tensile and flexural strength tests to examine the effect of those additives.

They concluded that using the additives individually did not enhance the flexural and tensile strength properties in high density cement. Moreover, additives known to improve flexural and tensile strengths properties in normal density did not work effectively in higher density and temperature cement systems.

Dai[15] (2002) presented a review on carbon nanotube structure. He presented all the aspects of carbon nanotube structure including its growth, dispersion of nanotubes, electrical and mechanical properties of nanotubes. Author highlights the importance of carbon nanotubes in the field of science and nanotechnology.

Hone[16] (2004) investigated the thermal properties of carbon nanotubes. Author discusses about the theoretical and experimental work on the specific heat of nanotubes. He found that thermal properties of CNT are dominated by phonons. He concluded that coupling between nanotubes in bundle is relatively weak.

Li et al.[17] (2007) investigated the micro-structure of cement reinforced by carbon nanotubes. Two types of cement composites were developed: one having treated (with acid) CNT and the other having untreated CNT. The micro-structure of both types of CNT-cement composite was analyzed by SEM. Mechanical strength of the treated CNT-cement composite was found to be higher than the untreated CNT-cement composite.

Reddy et al.[18] (2007) compared several methods for measuring cement shrinkage under various conditions including downhole. Cement shrinkage for environments where cement slurry is either closed to or open to external water sources was measured. API test methods were adopted for measuring cement shrinkage. Values obtained were discussed and modifications needed in the procedures were proposed for calculating volume changes due to cement shrinkage based on placement time, gel-strength development and shear strength.

Musso et al.[19] (2009) studied about the usage of non-functionalized MWCNT's in the cement composites which resulted in an increase in modulus of rupture by 35% and addition of functionalized MWCNT's in the cement composites resulted in the decrease in modulus of rupture by 40%.

Yu and Kwon[20] (2009) studied the effect of CNT on the mechanical strength of the cement having different dispersion techniques. They fabricated CNT-cement composites using two types of dispersion method: (a) acid-treatment method and (b) non-covalent dispersion. They found out that CNT-cement composites fabricated by acid-treatment method showed relatively higher strength than that of the plain cement and CNT-cement fabricated by non-covalent dispersion.

Ghasemzadeh and Jalalabad[21] (2011) developed an analytical method which was based on the properties of CNT-cement composite. They assumed CNT as transversely isotropic and were dispersed in the cement matrix uniformly.

Nochaiya and Chaipanich (2011) investigated the hydration effect of MWCNT's on the cement paste and concluded their results by SEM micrographs that MWCNT's and cement paste have good interaction between them and it acts as filler in the cement matrix. Authors also investigated the effects of MWCNT's upon the microstructure and porosity of OPC. They found that the addition of 0.5% or 1% wt MWCNTs significantly reduced the number of mesopores with diameters around 10 nm-50 nm. But MWCNTs addition did not influence the number of macro pores and resulted in only modest reduction in total porosity.

Ozyildirim, Zegetosky (2011) performed exploratory investigation of nanomaterial to improve strength and permeability of concrete. This study evaluates the use of a variety of nano-materials in concrete compared with conventional concrete and concrete containing common SCMs. The potential benefits of using nano-materials over other SCMs are high reactivity and cost-effectiveness; in addition, smaller amounts are necessary, resulting in less cement replacement. Concretes containing nano-silica and nano-alumina were prepared in the laboratory. They were compared with concretes containing silica fume, fly ash, slag, or only portland cement. Specimens were tested for compressive strength and permeability.

The microstructure of selected concretes with improved compressive strength and permeability was analyzed by using an atomic force microscope and nano-indenter to

explain the improvements. The results of this study indicate that some of the nano-materials tested have potential in concrete applications.

Sobolkina et al. (2012) investigated the effect of an efficient dispersion of CNT in the cement which leads to an evenly distributed stresses in the cement matrix and improved mechanical properties. Authors concluded in their study that an efficient dispersion of the CNT's into the cement matrix can result in 40% increase in the compressive strength.

Han et al. (2012) studied about the general transport properties (i.e. water sorptivity, water permeability and gas permeability) of CNT-OPC composites and the results indicated that at even small dosage of MWCNT there is a decrease in the water sorptivity coefficient, water permeability coefficient and gas permeability coefficient.

Rahimirad and Baghbadorani (2012) investigated carbon nano tube on Portland cement and investigated that there is upto 70% increase in the compressive strength with the addition of 0.05 wt% of cement.

Roij et al. (2012) investigated the effect of nano-material on oil well cement. They did a comparative research between the samples of API Class G cement mixed with patented active nano-material and simple API Class G cement. Their results indicated that nano-engineered cement showed higher values of compressive strength relative to the simple G class cement.

Santra et al. (2012) explained the influence of Nano materials in oil-well cement hydration and mechanical properties. They concluded that concrete strength improvement as a result of the addition of small-size nano-silica is much higher than that of silica fume, even though the quantity used is much smaller for the former.

Stronger bonding between aggregates and cement paste matrix increased compressive and/or tensile strength decreased permeability and hence increased resistance to calcium leaching and various types of chemical attack and more uniform microstructure with reduced pore size and volume. However, the difficulty associated with uniformly dispersing the nano-silica increases with its quantity and specific surface area, which is especially more apparent when a low water-to-cementitious-materials ratio is used.

2.8 HYDRATION OF CEMENT SLURRIES

Portland cement consists of five major compounds and a few minor compounds. The composition of a typical Portland cement is listed by weight percentage in **Table 2.3**.

Table 2.3: Composition of Portland Cement with chemical composition and weight percent (Roij, Egyed & Lips, 2012)

Cement Compound	Symbols	Weight Percentage	Chemical Formula
Tricalcium silicate	C_3S	50	$3Cao.SiO_2$
Dicalcium silicate	C_2S	25	$2Cao.SiO_2$
Tricalcium aluminate	C_3A	10	$3Cao.Al_2O_3$
Tetracalcium aluminoferrite	C_4AF	10	$4CaO.Al_2O_3$
Gypsum	-	5	$CaSO_4.2H_2O$

When water is added to cement, each of the compounds undergoes hydration and contributes to the final product. Only the calcium silicates contribute to strength. Tricalcium silicate is responsible for most of the early strength during first 7 days. Dicalcium silicate, which reacts more slowly, contributes only to the strength at later times.

The equation for the hydration of tricalcium silicate is given by:

Tricalcium Silicate + Water ---> Calcium Silicate Hydrate + Calcium Hydroxide + Heat

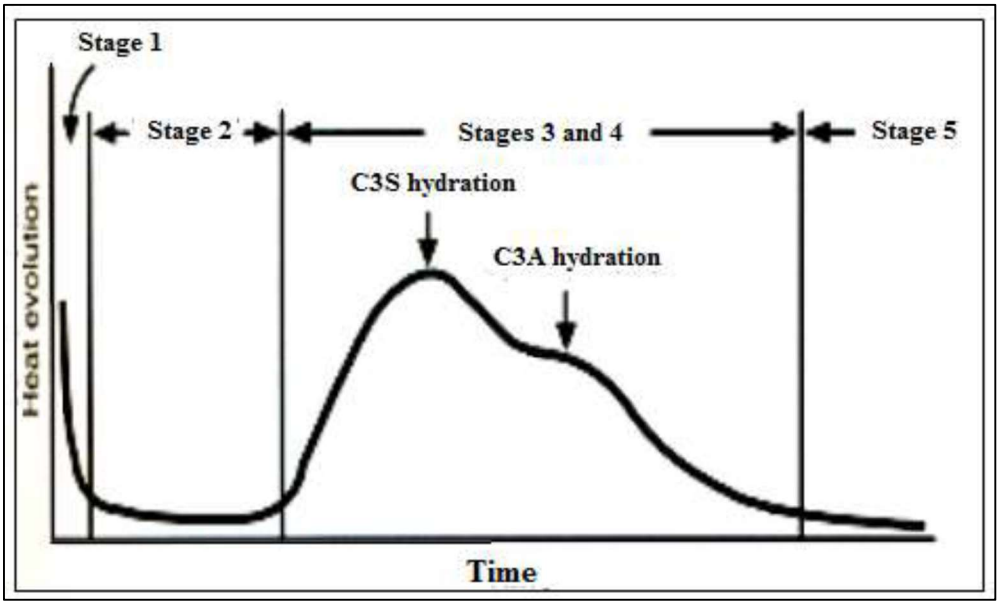

Figure 2.3: Schematic representation of hydration of Portland cement (Michaux & Nelson, 1990)

After adding water, tricalcium silicate quickly reacts to discharge calcium ions, hydroxide ions, and enormous amount of heat. The pH rapidly increases over 12 because of the discharge of alkaline hydroxide (OH^-) ions. This initial hydrolysis decelerates rapidly with a resultant decrease in heat (see Figure 2.3)

The reaction slowly continues to produce calcium and hydroxide ions until the system becomes saturated. Once this occurs, the calcium hydroxide starts to crystallize. Simultaneously, calcium silicate hydrate begins to form. Ions precipitate out of solution accelerating the reaction of Tricalcium silicate to calcium and hydroxide ions. The evolution of heat is then dramatically increased again. The formation of the calcium hydroxide and calcium silicate hydrate crystals provide "seeds" upon which more calcium silicate hydrate can form. The calcium silicate hydrate crystals grow thicker which makes it more difficult for water molecules to reach the anhydrate Tricalcium silicate. The speed of the reaction is controlled by the rate at which water molecules diffuse through the calcium silicate hydrate coating. This coating thickens over time causing the production of calcium silicate hydrate to become slower and slower.

The setting and hardening of OWC slurry are the result of a series of simultaneous and consecutive reactions between water and the constituents of the cement. Vlachou and Piau (1997) studied the microstructural and chemical evolution of Class G OWC slurry from the first minutes after mixing the cement powder with water until the beginning of setting. Based on scanning electron microscopy (SEM) and X-ray Diffraction (XRD), it was concluded that the form and structure of the hydration products were a function of experimental conditions, such as hydration time since mixing, stirring conditions (Vlachou and Piau, 1997), temperature (Justness et al., 1995), chemical composition of cement and additive used (Vidick, 1989) etc. The slurry hydrated under continuous stirring showed constant viscosity and adequate fluidity over several hours. The formation of small spheres of hydration particles of the aluminate phases had no

influence on the flow curve probably because these particles created no bonds between them and they moved freely into the inter-particle spaces.

Subsequently, the slurry thickened rapidly with the multiplication of hydrated crystals and the start of setting processes (Vlachou and Piau, 1997). On the other hand, slurries hydrated at rest showed a much more increase of viscosity during the first hours, after which the evolution process slowed down (Vlachou and Piau, 1997). It was reported that in case of slurries hydrated at rest, an over-saturation of ions in the grain neighborhood leads to the formation of aluminate hydration crystals of colloidal size (Vlachou and Piau, 1997). These crystal cover the surface of the grains and the hydration reaction eventually slows down. On the other hand, ions dispersed all over the sample volume and dissolution continues until saturation in case of slurries hydrated under stirring. The chemical composition of cement and additives used can affect the evolution of the chemical composition of the liquid phase of the cement paste (Michaux & Nelson, 1989). X-ray diffraction and scanning electron microscopy showed that a neat cement slurry changes from CSH(II), C_2SH_2, $C_3S_2H_3$ to dicalcium silicate hydrate (C_2SH) when the temperature exceeds 110°C and the microstructure of hardened slurry changes from a three-dimensional fiber network to a blank block or mass block for different curing temperature conditions (Zhang et al., 2008).

On the other hand, the major products of cement slurry with silica sands changes into $C_5S_6H_5$, C_6S_6H (> 150°C), $C_5S_5A_{0.5}H_{5.5}$, $C_{3.2}S_2H_{0.8}$ or other kinds of calcium silicate hydrate at high curing temperatures and the microstructures are transformed into a fiber network, rough frame network, short-parallel-needle fiber or mass block structure (Zhang

et al., 2008). Different cements show different sensitivity to additives, thus exhibiting different behaviors when mixed with the same additives (Vidick et al., 1989; Jupe et al., 2007). According to Justnes et al. (1995) only about 10% hydration is necessary for a plain API class G cement slurry with w/c = 0.5 to retain its shape at atmospheric pressure. Even though, changes in the hydration of C_3S with pumping time of cement slurries could not be correlated, it was found that the largest changes in pumping time as a function of temperature occurred in a temperature interval where ettringite/monosulphate decomposes and crystalline hydro garnet started to be formed (Jupe, 2005).

When the Nano-based product is used as additive, moisture remains necessary for hydration and hardening. The five major compounds of the hydration process of cement still remain the most important hydration products but the minor products of hydration probably change. Furthermore, the rate at which important hydration reactions occur and the relative distribution of hydration products changes as a result of the addition of the active Nano material. In addition, the crystallization of calcium hydroxide occurs at different rates and the reduction of heat generation from the hydration reactions takes place as well. More crystals form during these reactions and the relevant crystalline matrix is much more extensive.

When adding the Nano materials, the water changes chemically in sphere, electrical load, surface tension and reaches chemical/physical equilibrium in the matrix. This complex process depends on the type and mass of materials involved in the cement slurries. Similar to the chemical processes physical aspects are part of the equilibrium process in the matrix when the amount of water, trapped as free water is reduced and the crystals

grow into the empty void space. This makes the product less permeable to water and more resistant to all types of attack that are either water dependent or water influenced. A larger fraction of water is converted into crystalline water than is the case with the chemical reactions in the absence of the Nano material. The reduced porosity and increased crystalline structural matrix increases compressive, flexural and breaking strength of the product and change the relative ratios between these forces. Water continues to play a critical role, particularly the amount used in the initial phase of the hardening process. With conventional oil well slurries, the strength of the product increases when less water is used. The hydration reaction with added Nano material consumes a different amount of water, it is now also possible to use salt water and achieve satisfying results.

The porosity is still determined by the water to cement ratio but is affected to a lesser extent as a result of the increased rate and extent of the crystallization process. The extended crystallization process changes significantly with the active Nano material. The active Nano material causes a chemical physical equilibrium in the oil well cement slurry based on synergy between water percentage and API Class G oil well cement. The chemical reaction takes place based on water as a catalyst. As a result strong hydrogen bonds form which significantly contribute to the bonding forces. The binding mechanism changes from “glue” to “wrapping”. The cement slurry produces a crystalline structure that is able to partially block capillary pores. Because of this fibre- like structure it become flexible and prevents micro cracking to occur (De La Roij et. al, 2010).

CHAPTER 3

EXPERIMENTAL PROGRAM

Cement lab testing is the main way to evaluate and develop different properties of cement systems and to simulate the actual behavior of the cement in high pressure / temperature downhole environment.

The planned experimental program for this study is implemented according to the American Petroleum Institute (API) (API Specifications-10A, 2012) procedures and consists of several cement tests and each addresses to certain cement property. The properties of cement included in this research are:

a. Thickening Time
b. Density
c. Rheology
d. Free Water Separation
e. Compressive Strength Test
    - Compressive Strength by “Crushing” method
    - Compressive Strength by “Sonic” method
f. Microstructural Analysis
    - XRD
    - SEM

3.1 WELL SPECIFICATIONS

A cement design of typical well of Saudi Arabia has been selected to test the behavior of Carbon nanotube (CNT) on cement design performance. The specifications of well are given in Table **3.1** which have been acquired from a typical well of Saudi Arabia.

Table 3.1 : Typical Well Specifications

Well Parameters	Values
Depth of Well (TVD)	14000 ft
Bottom hole circulating temperature (BHCT)	228 °F
Bottom hole static temperature (BHST)	290 °F
Time to reach bottom (TRB)	49 min
Surface Pump Pressure	1050 psi
Mud Weight (MW)	85 PCF
Bottom hole pressure (BHP)	8265 psi

3.2 CEMENT SLURRY DESIGN

The particular well has a special cement system design since the well is deep with high pressure and temperature conditions. The selected cement system consists of different materials in which each material contributes and adds chemical and physical property to make the cementing job successful.

The **Table** 3.2 explains the cement slurry design of particular well without addition of Carbon Nanotubes (CNT).

Table 3.2 : Cement Slurry Design without Carbon Nanotube (CNT)

Properties	Values
Slurry Density (Approx.), PCF	125
Water Cement Ratio (WCR)	0.44
Slurry Yield	1.367
Thickening Time	4-5 hours
Class G cement powder + 35% silica flour + 1% expanding agent + 0.8% Dispersant + 0.2% Fluid loss control agent + 0.5% Fluid loss control agent + 1% Retarder + 1% Friction reducer + 0.25gm Defoamer	

A series of tests will be conducted on the slurry design without Carbon Nanotubes according to the experimental program results in the base slurry design which will be used as a reference. After the base cement slurry design, the Carbon Nanotube material

will be incorporated in the above cement slurry design in different percentages by weight of cement (0.1%, 0.25% & 0.5%) as Table 3.3 explains the cement slurry design in the presence of Carbon Nanotubes.

Table 3.3 : Cement Slurry Design with Carbon Nanotube (CNT)

Properties	Values
Slurry Density (Approx.), PCF	Unknown
Water Cement Ratio (WCR)	0.44
Slurry Yield	Unknown
Thickening Time	Unknown
Class G cement powder + 35% silica flour + X% CNT + 1% expanding agent + 0.8% Dispersant + 0.2% Fluid loss control agent + 0.5% Fluid loss control agent + 1% Retarder + 1% Friction reducer + 0.25gm Defoamer	

Where, X represents the Carbon Nanotube percentages (0.1%, 0.25% & 0.5%) BWOC.

3.3 MATERIALS

Cement slurries used in this study are prepared using high sulfate-resistant API Class G oil well cement with a specific gravity of 3.14. The chemical properties of simple class G cement are summarized in **Table** 3.4. All the cement slurries have been prepared using Tap water. A number of conventional chemical admixtures from Halliburton have been

used as the **Table** 3.5 explains the functions and concentrations of additives used in research.

Table 3.4 : Chemical Composition of Class G Cement

Chemical Component (%)	
Silica (SiO_2)	21.6
Alumina (Al_2O_3)	3.3
Iron Oxide (Fe_2O_3)	4.9
Calcium Oxide, Total (TCaO)	64.2
Magnesium Oxide (MgO)	1.1
Sulphur Trioxide (SO_3)	2.2
Loss on Ignition	0.6
Insoluble Residue	0.3
Equivalent Alkali (as Na_2O)	0.41
C_3A	<1
C_3S	62
C_2S	15
$C_4AF + 2C_3A$	16

Table 3.5 : Commercialized Additives with their functions and percentages

Additives	Functions	Concentration (%BWOC)
SSA-1	Strength Stabilizing Agent	35
MBHT	Extender	1
HR-12	Retarder	1
CFR-3	Friction Reducer	1
Halad-344	Fluid Loss Controlling Agent	0.2
Halad-413	Fluid Loss Controlling Agent	0.5
DA-3000	Anti-foaming Agent	0.25/10bbl

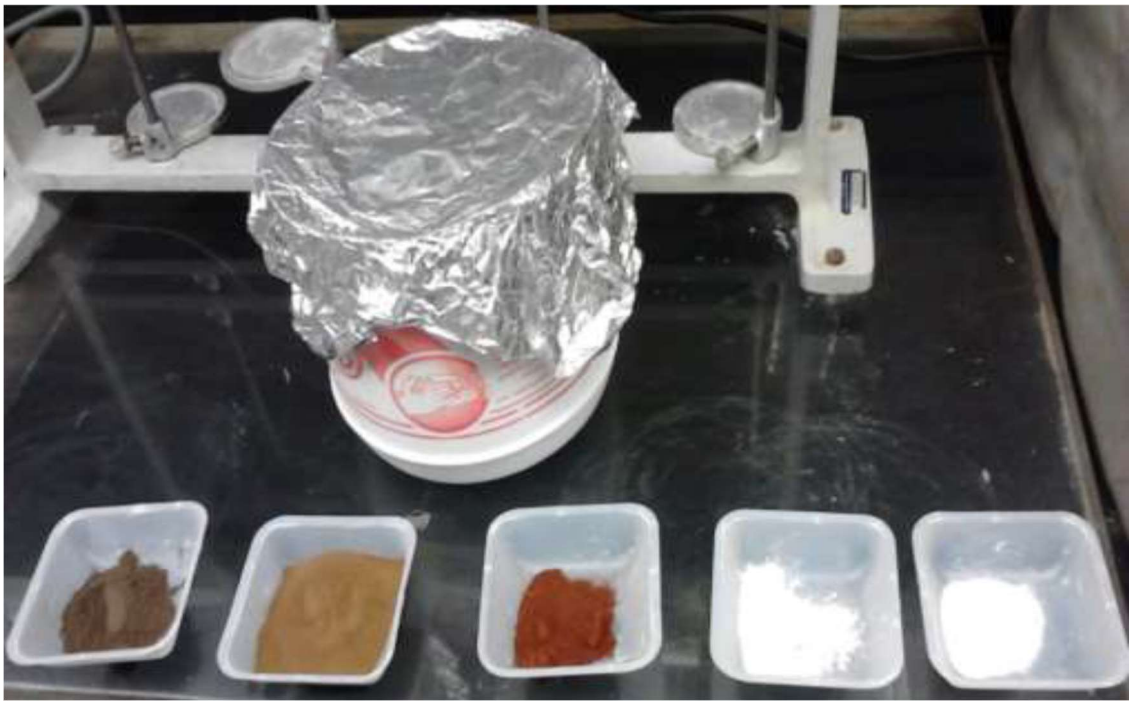

Figure 3.1: Additives used in Experiments

3.4 PROPERTIES OF CARBON NANOTUBES (CNT)

The unique structure and the nano scale of carbon nanotubes (CNTs) reduce the defects in their molecular structure as well as increase their surface-to-volume ratio. CNTs properties would open a wide door for many mechanical, electrical, thermal, and chemical applications. The applications for CNTs include structural and nonstructural applications. Examples for non-structural functions may include self-sensing for measurements of strain, temperature, damage, self-heating (for deicing), electromagnetic interference shielding, and even drug delivery for medical applications. For structural applications, the unique structure allows carbon nanotubes to have unique mechanical properties that make them promising reinforcements to many engineering materials.

The hexagonal structure of the carbon lattice in the CNTs provides a very strong structure that is stronger than diamond bonds. However, the van der Waals forces between the cylindrical tubes of the MWCNTs are much weaker, and hence will allow the inner tubes to slide with respect to each other.

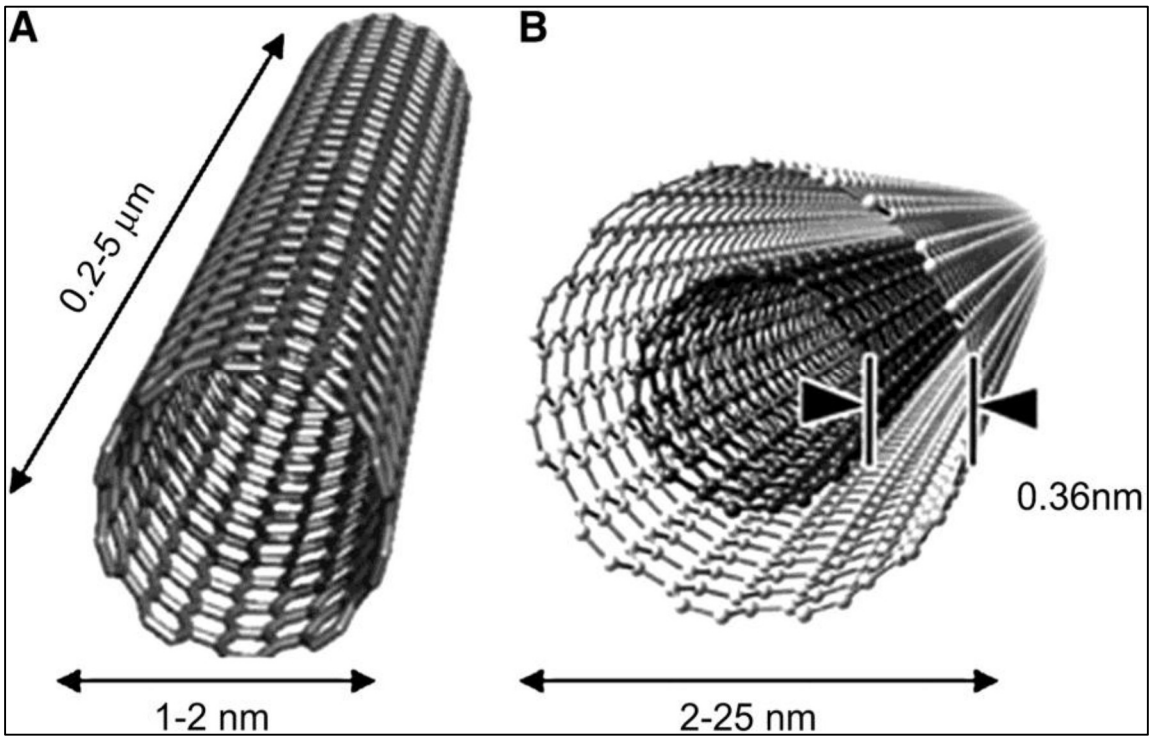

Figure 3.2: Explains the structure of Carbon Nano tubes

The measured tensile strength for multi-walled CNTs was reported to reach 63 GPa (about 100 times stronger than steel), with ultimate strain capacity of more than 12% (about 60 times higher ductility than steel) and with elastic Young's modulus of about 950 GPa. Wong, et al. have measured the flexural strength of MWCNTs fixed as a cantilever beam- using atomic force microscope (AFM) tip, the results show the capability of the MWCNT to elastically store and absorb strain energy. The average flexural strength reported was 14.2 ± 8.0 GPa. Yet, CNTs has a very low mass density which varies based on the purity from 0.037 g/cm3 like of the super growth CNTs, to about 1.3-1.4 g/cm3 in conventional CNTs (about 1/6 of the density of the mild steel).

3.5 CEMENT SLURRY PREPARATION

The preparation of cement slurry is important because of the effect of the shear history of the mixture on the properties of cement (Orban et al., 1986). The cement slurry is prepared using a variable speed high-shear blender type mixer with bottom drive blades as per the API Specifications (see **Figure** 3.5)

Figure 3.3: Silica flour powder

Two methods of mixing are present in API specifications. First method is dry mixing in which all the additives are blended dry in cement. Second method is wet mixing, in which all the additives are mixed in water before blended in cement. Both methods of mixing are applied for different well conditions and location.

Figure 3.4: Blending of cement with silica products prior mixing

In all experiments, wet mixing method has been implemented in which first of all, cement, water and additives are weighed subjected on the cement design. The cement and silica products are dry blended before mixing in water (see **Figure** 3.4). Tap water is used to mix the liquid and dry additives at low speed of 4000 RPM. The dry blended mixture of cement and silica products is put in water-additive mixture within 15 seconds. Now at a speed of 12000 RPM for 35 seconds, the whole slurry is mixed in high speed mixer. The cement slurry is then conditioned in atmospheric consistometer at 194 °F temperature for 20 minutes as shown in **Figure** 3.6. Now, this conditioned slurry can be used for preferred tests.

Figure 3.5: High Speed blender

Figure 3.6: Atmospheric Consistometer

3.6 THICKENING TIME TEST

This test explains the duration inside which cement slurry remains pumpable under well simulated conditions (Dwight, 1990). The laboratory test conditions should represent the time, temperature, and pressure to which cement slurry will be exposed during pumping operations. Other factors that can affect the slurry's pumpability during a job cannot be simulated exactly during a laboratory thickening time test (fluid contamination, fluid loss to formation, unforeseen temperature variations, unplanned shutdowns in pumping, etc.).The most commonly used apparatus incorporates a rotational cylindrical slurry container equipped with a stationary paddle assembly, all sealed off in a pressure vessel capable of enduring well-simulation pressures and temperatures (**Figure** 3.7, API Spec 10A). The slurry container is revolved at a speed of 150RPM. To determine the thickening time, the consistency of cement slurry is measured. The consistency, expressed in Bearden units of consistency (Bc), is determined by the force imposed by the slurry against the paddle and measured as a torque. A potentiometer, or its equivalent, is used to determine the torque.

First the cement slurry is prepared according to API Specifications. The prepared cement slurry is poured in HPHT consistometer cup and placed in HPHT consistometer. After placing, the test conditions are applied. During the thickening time test, increase the temperature and pressure of the cement slurry in the slurry container in agreement with the applicable well-simulation test program. Then the test is conducted up to the time at which the slurry reaches a consistency considered satisfactory to make it unpumpable (for

example 70 Bc or 100 Bc). The slurry consistency at which the thickening-time test was terminated should be documented and reported.

After that, the test is terminated and the consistometer is cooled before releasing the pressure. After releasing the pressure, the potentiometer and slurry container are removed and made ready for the next test.

Figure 3.7: HPHT Consistometer

3.7 DENSITY OF OWC SLURRIES

The density explains the hydrostatic head of cement slurry in a well. The preferred apparatus for measuring the density of cement slurry is the pressurized fluid density balance (**Figure** 3.8). By pressurizing the sample cup, any entrained air is decreased to a negligible volume, thus providing a slurry density measurement more representative of the true slurry density.

First the cement slurry is prepared according to API Specifications. The slurry is conditioned at atmospheric pressure and 194 °F temperature. After the conditioning of slurry, it is poured pressurized mud balance to get the density.

Figure 3.8: Pressurized Mud balance

3.8 FREE WATER CONTENTS

The free fluid test for testing cement slurries used to cement a well helps determine a slurry's capacity to prevent fluid separation in static conditions, both during placement and after it has been placed into the wellbore. Excessive free fluid in slurry can cause problems with water pockets, channeling, sedimentation, zonal isolation, etc. For the measurement of free water contents, the cement slurry is prepared and conditioned according to API specifications. After the conditioning of cement slurry, the cement is poured in graduated cylinder up to a mark and covered it with aluminum foil to prevent evaporation (see **Figure** 3.9). Later, it is subjected to 2 hours test duration. At the end of test duration, a syringe is used to extract the free water separated from the cement slurry and the amount of water is measured in milliliters (ml).

Figure 3.9: Graduated Cylinder

3.9 RHEOLOGICAL PROPERTIES

The rheology determines the performance of cement and helps in determining the pump ability of cement. In rheology test, apparent flow properties (plastic viscosity, yield point, frictional properties, gel strength, etc.) of a cement slurry are determined, using a rotational viscometer such as HPHT Viscometer by Chandler at high temperature conditions (see **Figure** 3.10).

First of cement slurry is prepared and conditioned according to API specifications. The conditioned slurry is poured in pre-heated cylinder of viscometer at 194 °F test temperature. The viscometer is run at different shear rates and at the end of test, in built software is used to compute the results of plastic viscosity and yield point.

Figure 3.10: HPHT Viscometer

The gel strength of a fluid may be measured immediately after determining the rheological properties of the sample or on a separate, freshly-prepared fluid.

First, reconditioning the fluid in the viscometer is done for 1 min at 300 RPM to disperse the gels and to get better measurement of the gel strength. For tests on separate fluids, the cement slurry is prepared, conditioned and loaded in the viscometer. The fluid is then conditioned for 1 min at 300 RPM. Rotor is stopped and slurry is kept static for 10 seconds in viscometer. At the end of 10 seconds, the rotation is resumed at 3 RPM, the maximum deflection obtained is called initial gel or 10 sec gel strength. After this, cement slurry is kept static for 10 minutes, then after resuming, the maximum dial deflection is reported as the 10-min gel strength.

3.10 COMPRESSIVE STRENGTH OF CEMENT

The compressive strength properties determine the integrity of cement and its ability to bear long term imposed stresses (Adam, 1986). The maximum pressure used for curing is normally 3,000 psi (API), unless otherwise specified. There are two methods to measure the compressive strength, first by crushing and other is by non-destructive method. Compressive strength tests are conducted according to the API Specifications (API Specification-10A, 2012).

3.10.1 Compressive Strength by Crushing Method

The crush strength test indicates the strength of cement slurry after it has been pumped into the well and allowed to set static. The slurry is subjected to temperature (and

normally, pressure) for various lengths of time. The strength test may be performed at bottomhole conditions or the conditions at a specific point of interest (at the top of a long cement column, at the top of a liner, across a producing zone, etc.).

In this test, first of all, the cement slurry is prepared and filled in the chambers of the prepared moulds (**Figure** 3.11), covered with the top plate, and immediately placed in a curing vessel at the desired test initiation temperature (normally 27 °C). Heat and pressure in accordance with the test schedule are applied. In this particular case, test molds are subjected to the test conditions of 290°F temperature and 3000 psi pressure for 24 hours in HPHT curing vessel (see **Figure** 3.12) . At the end of test duration, the molds with set cement (see **Figure** 3.13), are removed and cubes are detached from molds (see **Figure** 3.14). Later, the cubes are crushed in compressive strength tester to get compressive strength results (see **Figure** 3.15).

Figure 3.11: Cement Moulds

Figure 3.12: HPHT Curing Machine

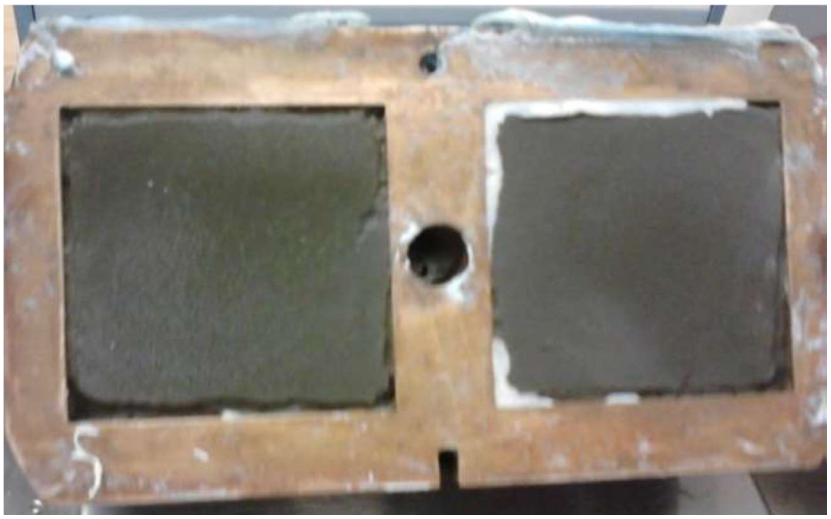

Figure 3.13: Cured Cement moulds

Figure 3.14: Cured Cubes of Cement

Figure 3.15: Crushing of cement cubes using compressive strength tester

3.10.2 Compressive Strength by Sonic Method

The sonic strength (UCA analyzer) test is a non-destructive test performed on cement slurry to estimate its strength. Correlations have been developed to approximate the compressive strength of a cementing composition based on the time required for the ultrasonic signal to pass through the cement as it sets. Sonic strength and crush strength indications can vary considerably, depending on the temperature of the test, slurry composition, etc.

The sonic compressive strength of cement slurry is measured by placing slurry in autoclave unit of ultrasonic cement analyzer (UCA) (**Figure** 3.16) with temperature and pressure adjusted to simulate downhole conditions. An acoustic signal is then transmitted through the cement sample. As the strength of the cement increased over time, the faster the acoustic signal travels through the sample.

First, the cement slurry is prepared and conditioned in atmospheric consistometer for 20 minutes at 150RPM. At the end of conditioning, the cement slurry is poured in the cell of ultrasonic cement analyzer (UCA) (see **Figure** 3.17). The cell is inserted in UCA and applied the test conditions as per the schedule set. Each test is conducted for 48 hours. At the end of test duration, the system is cooled and cement sample is removed from the cell.

Figure 3.16: Ultrasonic Cement Analyzer

Figure 3.17: Ultrasonic Cement Analyzer Cell

3.11 PERMEABILITY & POROSITY TESTS

Permeability determines the ability of fluid to flow at different pressure and helps in determining the long term performance of cement. The cement sheath is supposed to seal the zones and prevents fluid migration under HTHP conditions, which is only possible if we have low permeability. Porosity determines the void spaces where fluid is stored and later affects the properties of cement sheath.

The 1″×1″ cylindrical cement plugs are drilled out from the cubes of cement as shown in **Figure** 3.18. The cement plugs are dried for a day. After that, gas permeability and porosity tests are conducted on the Automated Porosimeter/Permeameter (**Figure** 3.19) at 500psi confining pressure.

This Automated Porosimeter/Permeameter (AP-608) is a state of the art system for measuring gas permeability and porosity of rock core samples under realistic reservoir conditions. The AP-608 comes complete with manually loaded hassler type coreholder and inserts for either 1.5″ or 1.0″ of diameters are supplied.

The permeability measurements are made using an unsteady state pulse decay technique. The permeability range of the AP-608 is from 5000md to 0.001md.

Figure 3.18: Cement Plugs

Figure 3.19: Automatic Porosimeter/Permeameter

3.12 MICROSTRUCTURAL ANALYSIS

The microstructure of cement slurry is studied using both SEM and XRD analysis. SEM explains the composition, topography and pore structure and XRD is a well-known technique for studying cement composition and hydration. Using XRD spectra, several compounds in hydrated cement paste such as alite (C3S), belite (C2S), ettringite (AFt), calcium hydroxide (CH, portlandite) and calcium silicate hydrate(C S-H), tobermorite etc. can be detected. For the XRD analysis, the cement samples are crushed to powder form and in SEM analysis, the small pieces of cement samples are used.

CHAPTER 4

RESULTS AND DISCUSSIONS

This chapter describes the results of study on the effect of Carbon Nanotubes on Portland Saudi cement type 'G' properties in high pressure and temperature applications. The results of each experimental test are discussed here for the proposed Carbon Nanotube percentages of the selected well cement systems.

4.1 EFFECT OF CARBON NANOTUBE ON THICKENING TIME

Thickening time test determines the time period in which slurry remains pumpable. This test was conducted using HPHT consistometer according to API specifications (2012). The pressure was set at 64MPa and the temperature at 228oF. The time for heating rate was 42 minutes. The four cement systems having Carbon Nanotubes percentages of (0%, 0.1 %, 0.25 % & 0.5%) BWOC were subjected to thickening time test and time of cement slurries to reach a consistency of 100 Bc were recorded. **Figure 4.5** explain the thickening time results of (0%, 0.1%, 0.25% & 0.5%) BWOC Carbon Nanotube cements systems. It is investigated that all four cement systems have (60, 110, 80 & 90) Bc consistencies at the start of tests which indirectly represent the viscosities at the start of test **(**see **Figure 4.6)**. When the test conditions are implemented, the viscosities are

reduced and stabilized for some period of time until 100Bc consistency achieved where they are considered unpumpable.

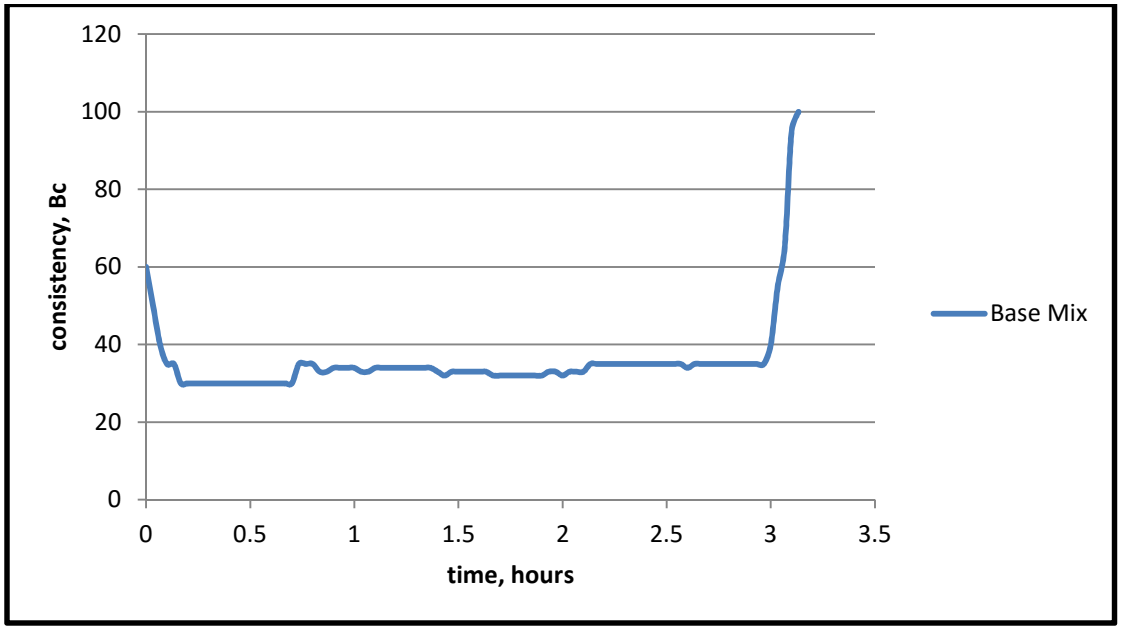

Figure 4.1: Thickening time plot of base mix (0% Carbon Nanotube)

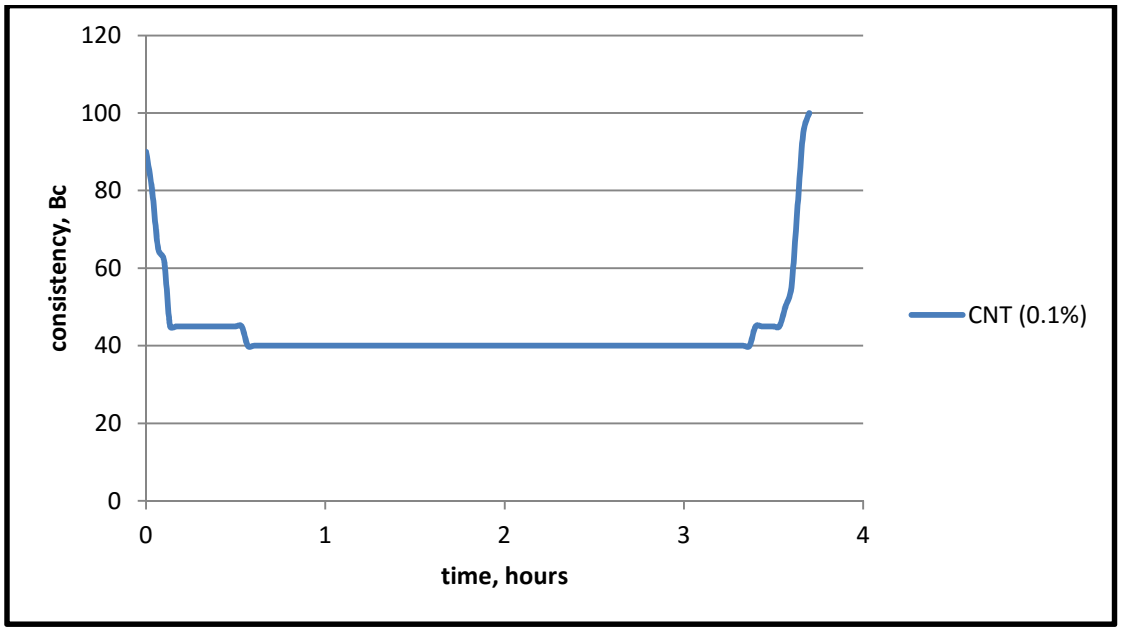

Figure 4.2: Thickening time plot of 0.1 % Carbon Nanotube cement slurry

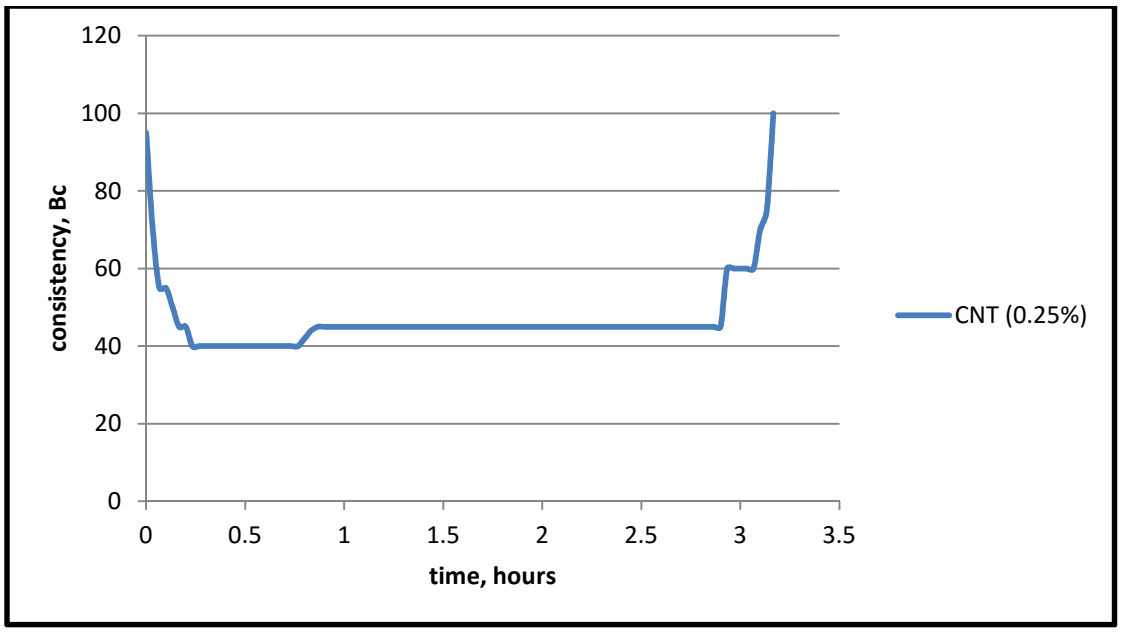

Figure 4.3: Thickening time plot of 0.25% Carbon Nanotube cement slurry

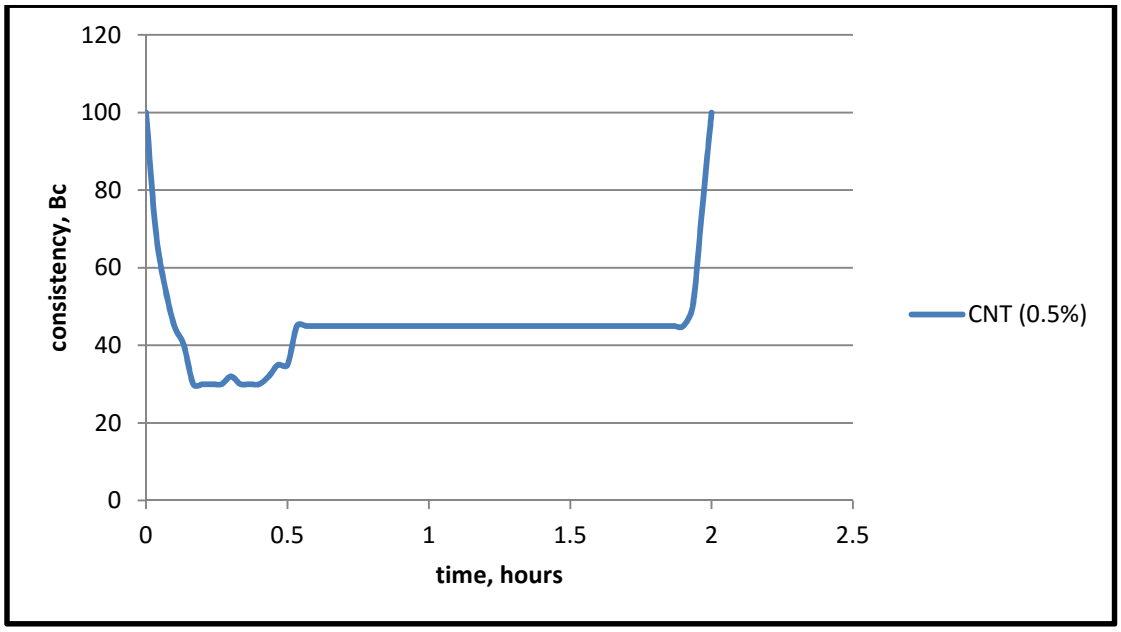

Figure 4.4: Thickening time plot of 0.5% Carbon Nanotube cement slurry

Figure 4.5 explains the thickening time test plot of all cement systems containing (0, 0.1, 0.25 & 0.5) % BWOC Carbon Nanotubes. It is observed that addition of lower percentages of CNT resulted in an increase in thickening time of slurries. The addition of higher percentage of CNT increases the hydration of cement and accelerates the cement slurries as it can be perceived that 0.5% CNT system achieved its thickening time only in 2 hours which is 1 hour before the base mix. The addition of 0.25% CNT increases the thickening time from 3 hours, thickening time of base slurry, to 3.3 hours. The further reduction in percentage of CNT by 0.1% BWOC increases the thickening time around 3.6

hours. So, it can be evaluated that CNT acts as retarder at lower percentages that helps in deep well cementing by retarding the thickening time.

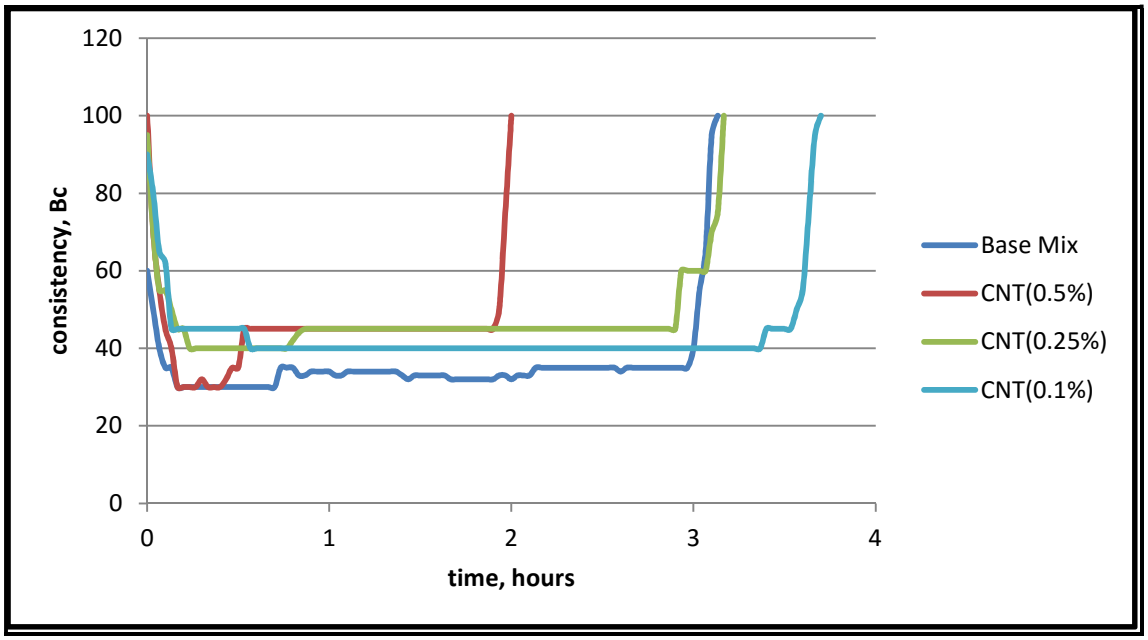

Figure 4.5: Variation of thickening time at different CNT concentrations (0, 0.1, 0.25 & 0.5) % BWOC

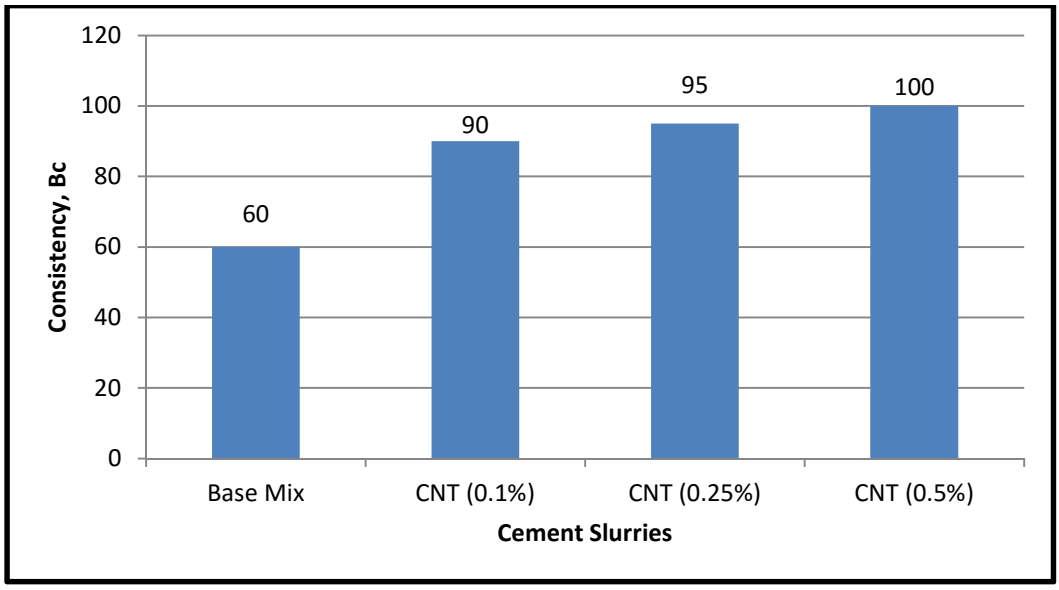

Figure 4.6: Consistencies at the start of test

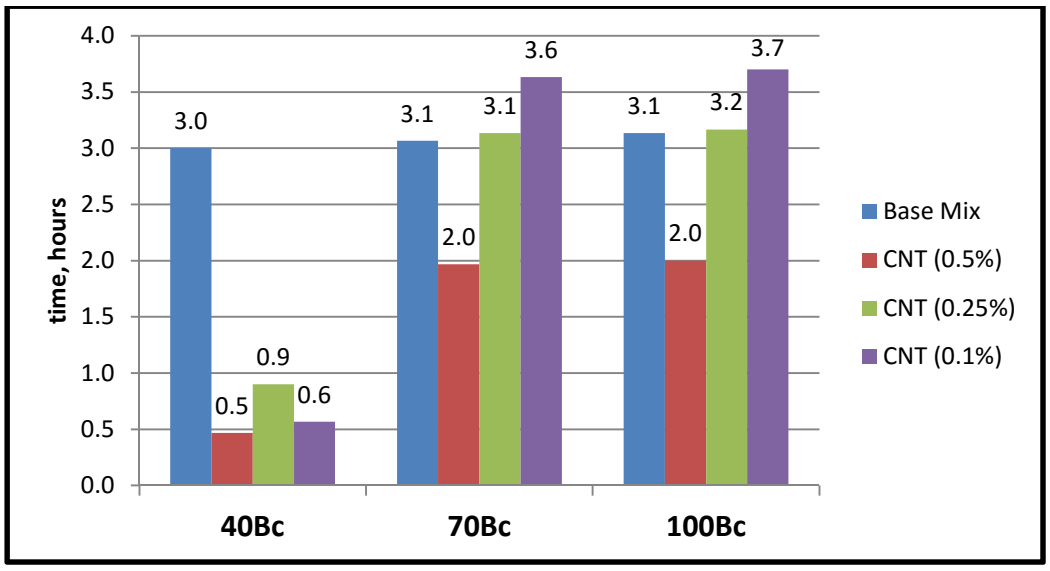

Figure 4.7: Time to reach 40Bc, 70Bc and 100Bc consistencies

From **Figure** 4.7, it can be investigated that it takes short time to achieve 40Bc consistency for all slurries with CNT but it takes very long time to achieve 70Bc consistency for all slurries. When all slurries approach 70Bc then time to get 100Bc is very short in all cement mix. This point is called right angle set as it takes minimum time to reach 100Bc consistency. So, it can be concluded that 70Bc is point after which slurries can be considered unpumpable because short time span between 70Bc and 100Bc.

4.2 EFFECT OF CARBON NANOTUBE ON FREE WATER SEPERATION

Free water is water that might be separated from the cement slurry and accumulated at top of cement while particles settling effect could take place.

To determine the effect of CNT on the amount of free water of cement slurry, the four cement systems having CNT percentages of (0 %, 0.1 %, 0.25 % & 0.5%) and simple Class G cement have been subjected to free water test where they have been aged for 2 hours under normal room temperature and atmospheric pressure. From Error! Reference source not found. results, it is evident that simple Class G cement cannot be injected alone in high pressure and temperature wells as it causes the free water separation at the top of cement which results in particle settling and low hydrostatic pressure of cement column. It is necessary to incorporate the additives in Class G cement to design slurry for HPHT wells. Later, 35% silica flour was mixed in simple class G cement and subjected

to free water content test. It was observed only addition of silica flour resulted in no free water contents which showed ability of silica flour to absorb more water.

The cement systems are designed containing different percentages of CNT. When these systems are subjected to free water separation tests, they all show no water separation at the top of cement column (see **Figure** 4.8).

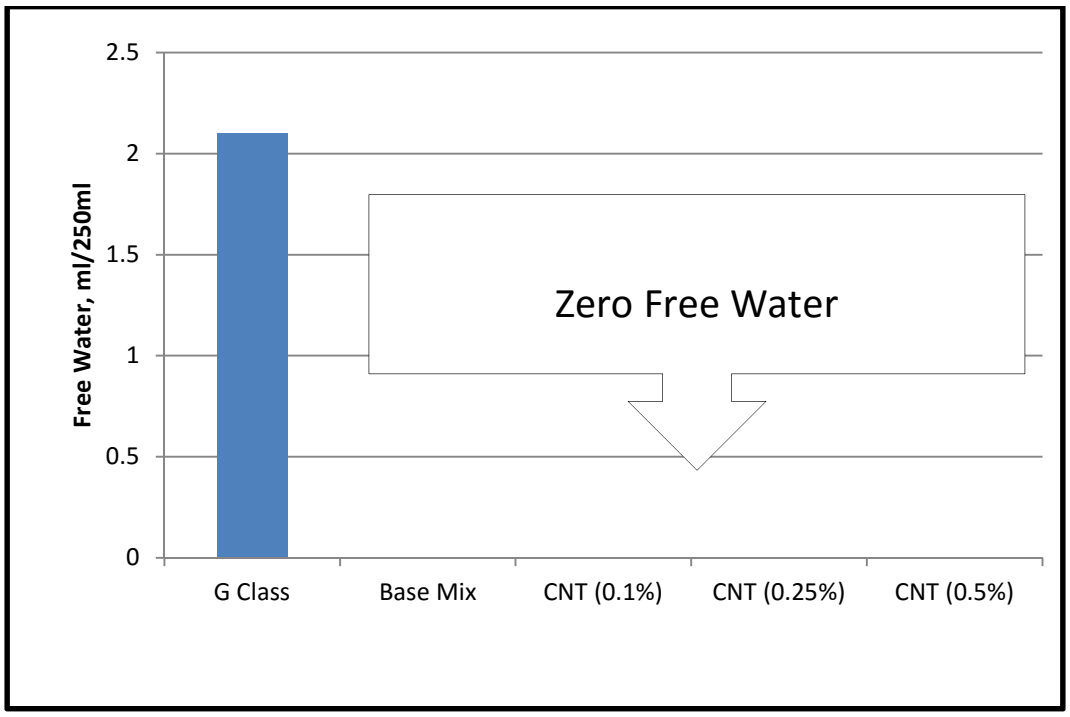

Figure 4.8: Free water content for different cement slurries

Table 4.1: Variation of Free Water contents of cement slurries containing (0%, 0.1%, 0.25% & 0.5%) CNT

Cement Slurries	Free Water (ml/250ml)
G class	2.1
G class + 35% SF	0
Base Mix	0
0.1 % CNT	0
0.25 % CNT	0
0.5 % CNT	0

4.3 EFFECT OF CARBON NANOTUBE ON DENSITY

The density of neat cement slurry, i.e., mixture of water and cement, varies from 1773 kg/m3 (110 lb/ft3) to 1965 kg/m3 (123 lb/ft3) depending on the API Class of the cement and the water/cement ratio (w/c). Higher density cement slurry may be required to control well fluids subjected to high bottomhole formation pressures. It is required to increase the density of OWC slurries to diminish the diffusion of heavy drilling muds. The density of the cement slurry is usually measured by pressurized mud balance in the laboratory. The cement slurry is designed with reference of 16.6lb/gal cement slurry of the selected well. The Carbon Nanotubes admixed cement slurries are subjected to density measurements. The densities of four cement slurry systems having (0%, 0.1%, 0.25% & 0.5%) Carbon Nanotube percentages and Class G cement slurry are measured in the laboratory (see **Table** 4.2).

Table 4.2 : Densities of slurries having (0%, 0.1%, 0.25% & 0.5%) CNT

Slurry Type	Density (lbs/gal)
Class G	15.8
Base Mix	16.7
0.10 % CNT	16.3
0.25 % CNT	16.5
0.50 % CNT	16.8

The density of cement slurry can be controlled by either water cement ratio or weighing agents. Depending on the selected well conditions, the Class G cement does not give required density to bear the pressure of deep wells. So different additives are added in class G cement to design required slurry (base mix). The density of base mix is calculated to be 16.7 lb/gal. Incorporation of lower percentages of CNT in base cement design decreases the density of cement slurry. But higher percentage of CNT (e.g 0.5%) increases the density of cement slurry as compared to the base mix. Addition of lower percentage of CNT (0.1% & 0.25%) does not reduce the density value appreciably as the density of cement slurry having 0.1% CNT is just reduced by 2.25% from the base cement of 0% Carbon Nanotube. Even the increase in the density of the cement slurry at 0.5% CNT is not very high. So it proves that addition of Carbon Nanotube material does not put noticeable effect on the density of cement as shown in **Figure** 4.9**.**

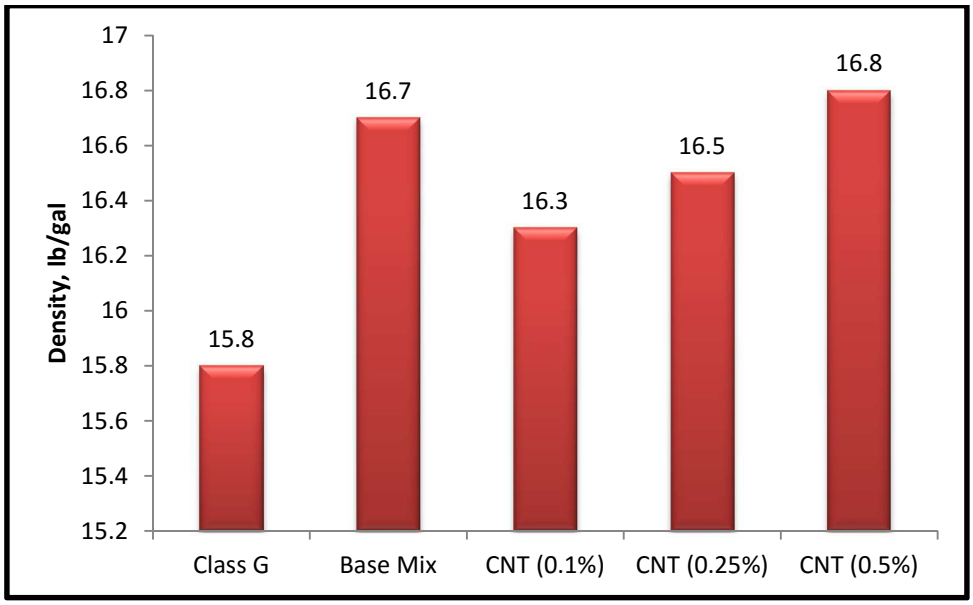

Figure 4.9: Density variation on addition of different Carbon Nanotube percentages

It should also be noted that density values reported here might be subjected to human measurement skills or density balance calibration accuracy.

4.4 EFFECT OF CARBON NANOTUBE ON COMPRESSIVE STRENGTH

The compressive strength properties measure the integrity and stability of cement to sustain long term imposed stresses. Cement slurry is supposed to develop the compressive strength early and make strong bond with walls of well after the placement. So that the drilling operations can be resumed in short time. The pumping of cement efficiently, placing it safely on time, assuring cement integrity after placement (prior to resuming drilling operation) are all issues to be considered. Therefore, compressive

strength tests are conducted to evaluate the development of cement strength with time utilizing the ultrasonic cement analyzer (UCA) and also to determine cement bonding stability after set utilizing the conventional compressive strength test (Crushing).

4.4.1 Non-Destructive Compressive Strength by Ultrasonic Cement Analyzer

The four cement systems having Carbon Nanotubes percentages of (0 %, 0.1 %, 0.25 % and 0.5%) and class G cement have been subjected to the ultra-sonic cement analyzer (UCA) test conducted under high temperature (290 °F) and pressure (4900 Psi) for 48 hours.

By Ultrasonic cement analyzer method, three different properties of cement slurries can be evaluated such compressive strength (green), transit time (blue) and acoustic impedance (aqua) on the chart.

When cement slurry is subjected to high temperature and pressure conditions, it starts developing its compressive strength with time. As cement develops compressive strength, it transit time reduces and its acoustic impedance starts increasing. Transit time and acoustic impedance properties help in cement bond logging and in determining cement bond with formation and casing.

From the test results, it is evident that when simple Class G cement is subjected to high temperature and pressure conditions, the compressive strength development is very high at the start which shows the fast hydration and setting of Class G cement. This development of compressive strength does not stay longer as after 12 hours the rise in compressive strength is quite low and it gets stable till the end of 24 hours (see

Figure 4.10). So it can be concluded that when Class G cement is subjected to high temperatures in excess of 230°F, the hydrated Portland cement undergoes significant phase changes which results in substantial decrease in compressive strength of the cement slurry. The cementing of deep wells with high temperature and pressure conditions requires the addition of special materials in the cement slurry to counteract the degradation of compressive strength. To combat strength retrogression in cement sheath and to reduce permeability at high temperature, silica flour in the range of 30%-40% is added to Portland cement (Iverson et al. 2010).

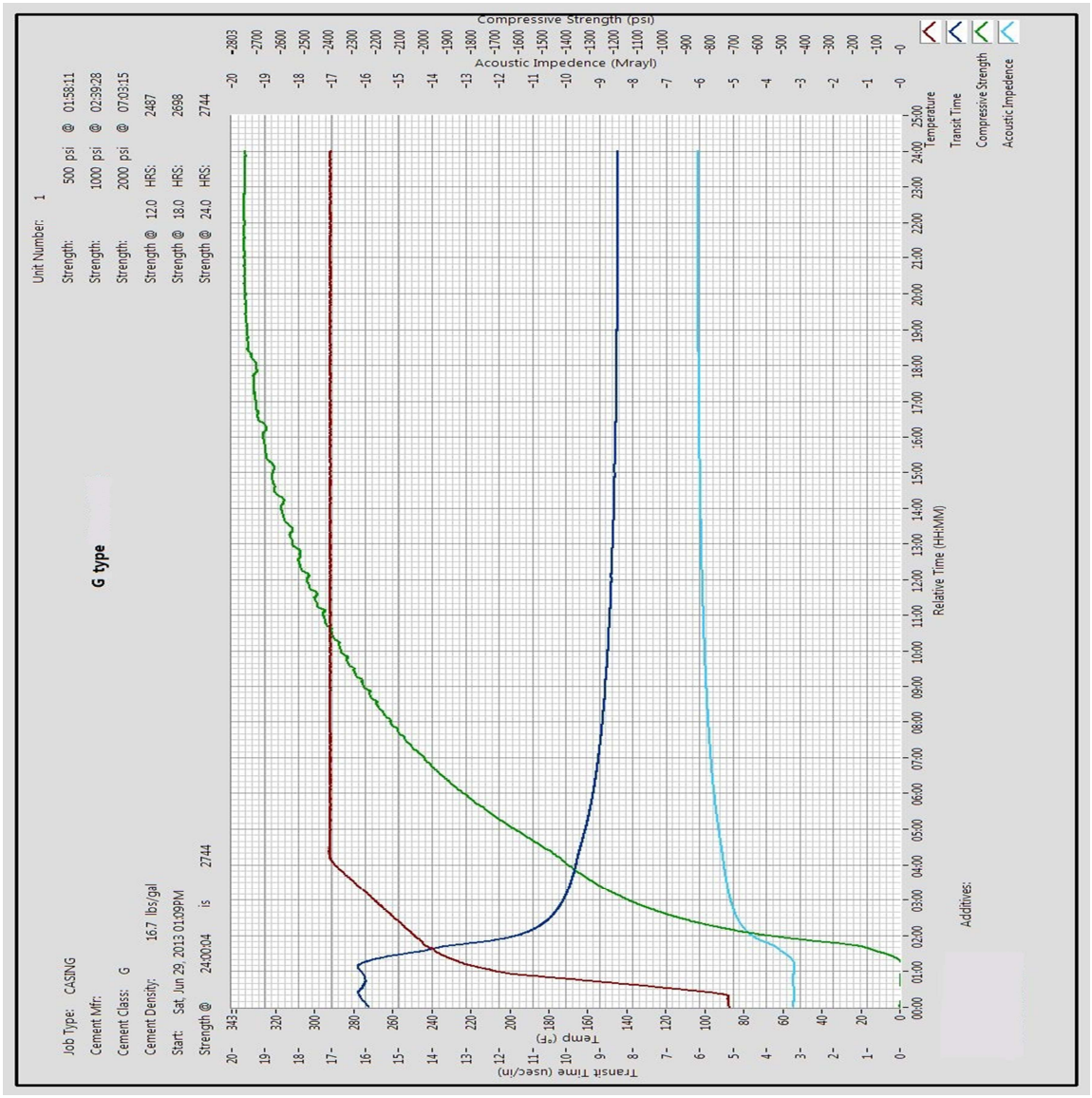

Figure 4.10: Compressive Strength development of simple class G cement at HPHT

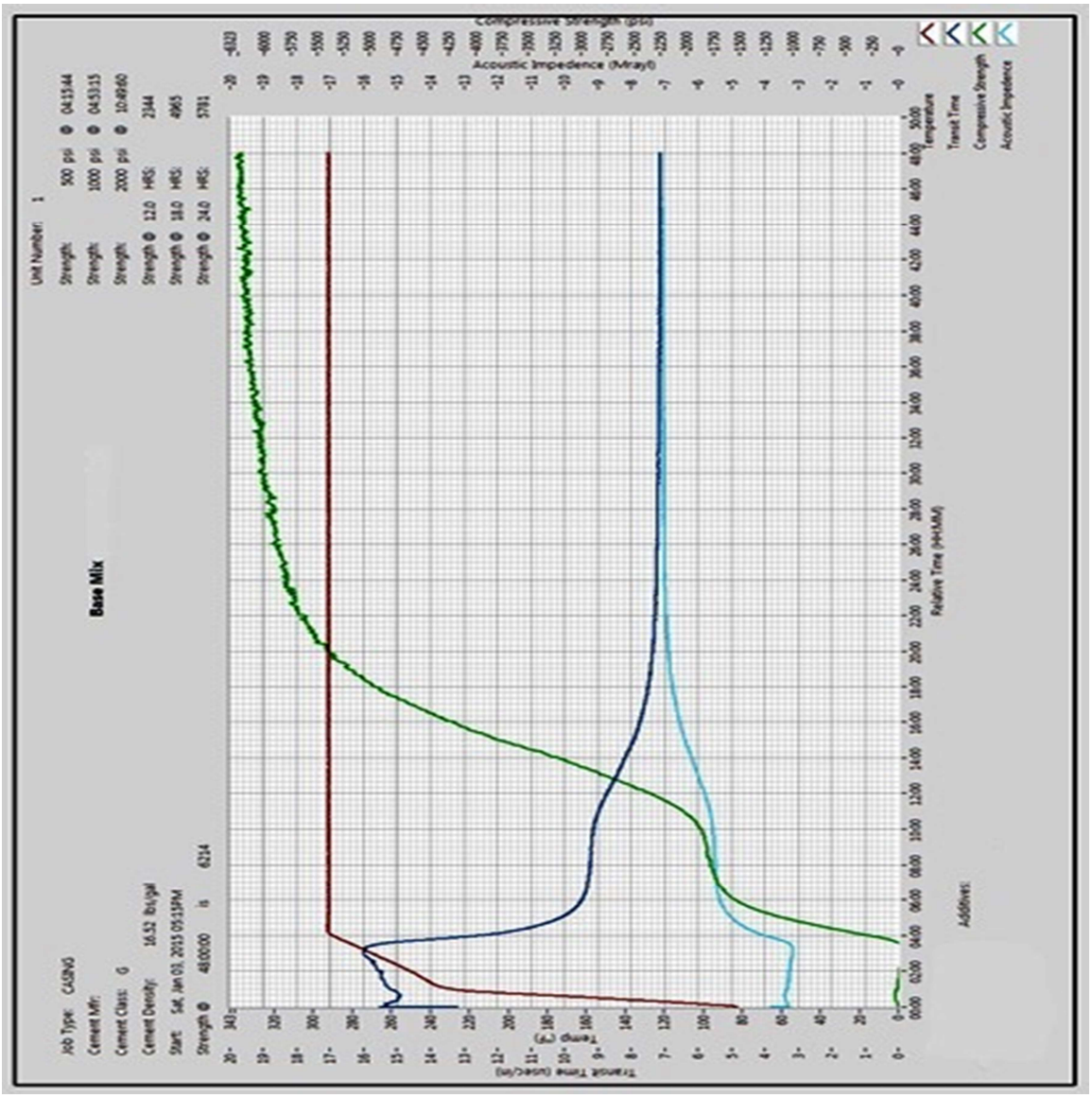

Figure 4.11: Compressive strength development of Base Mix (0% CNT) cement slurry at HPHT

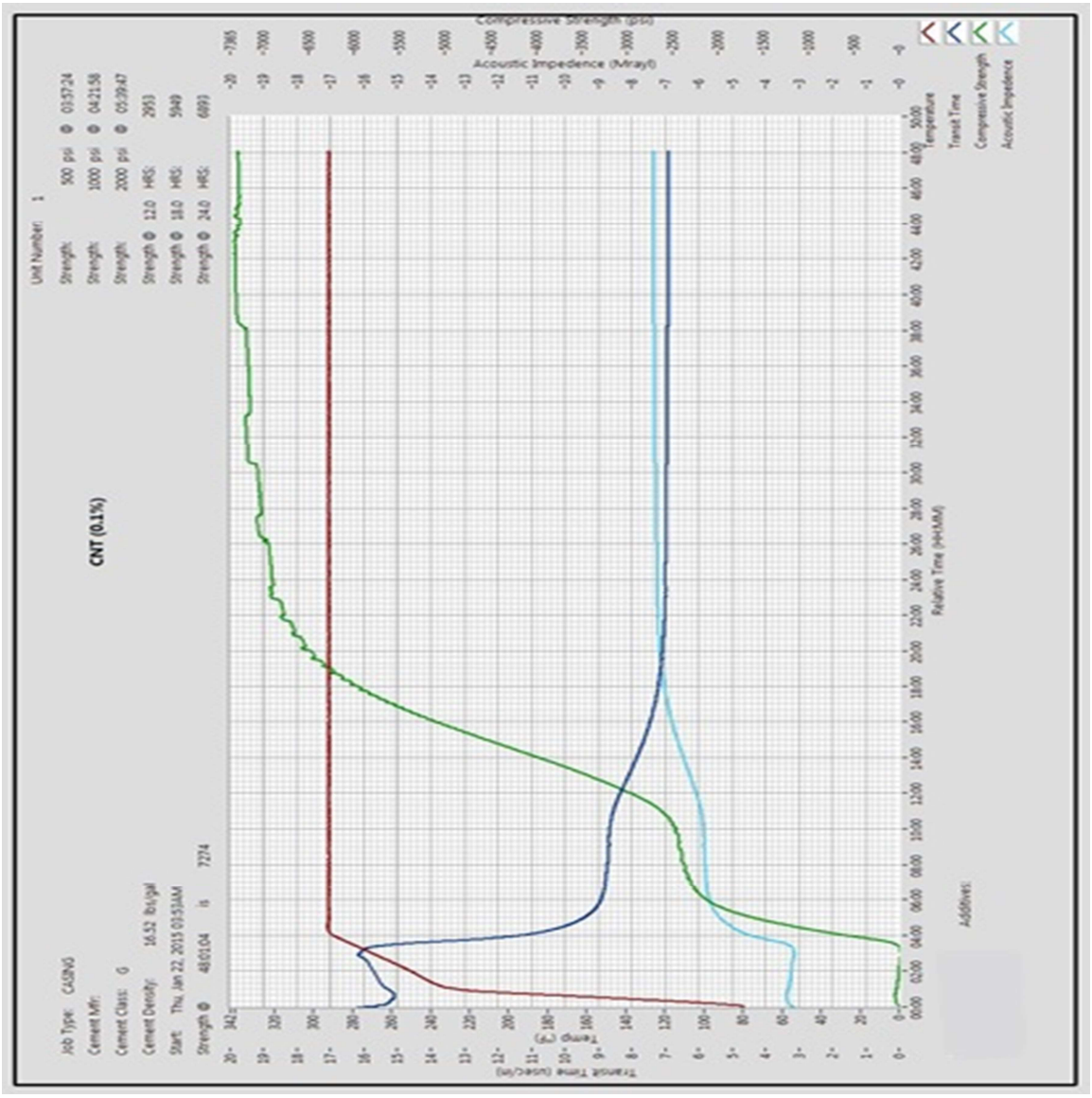

Figure 4.12: Compressive Strength development of 0.1% CNT cement slurry at HPHT

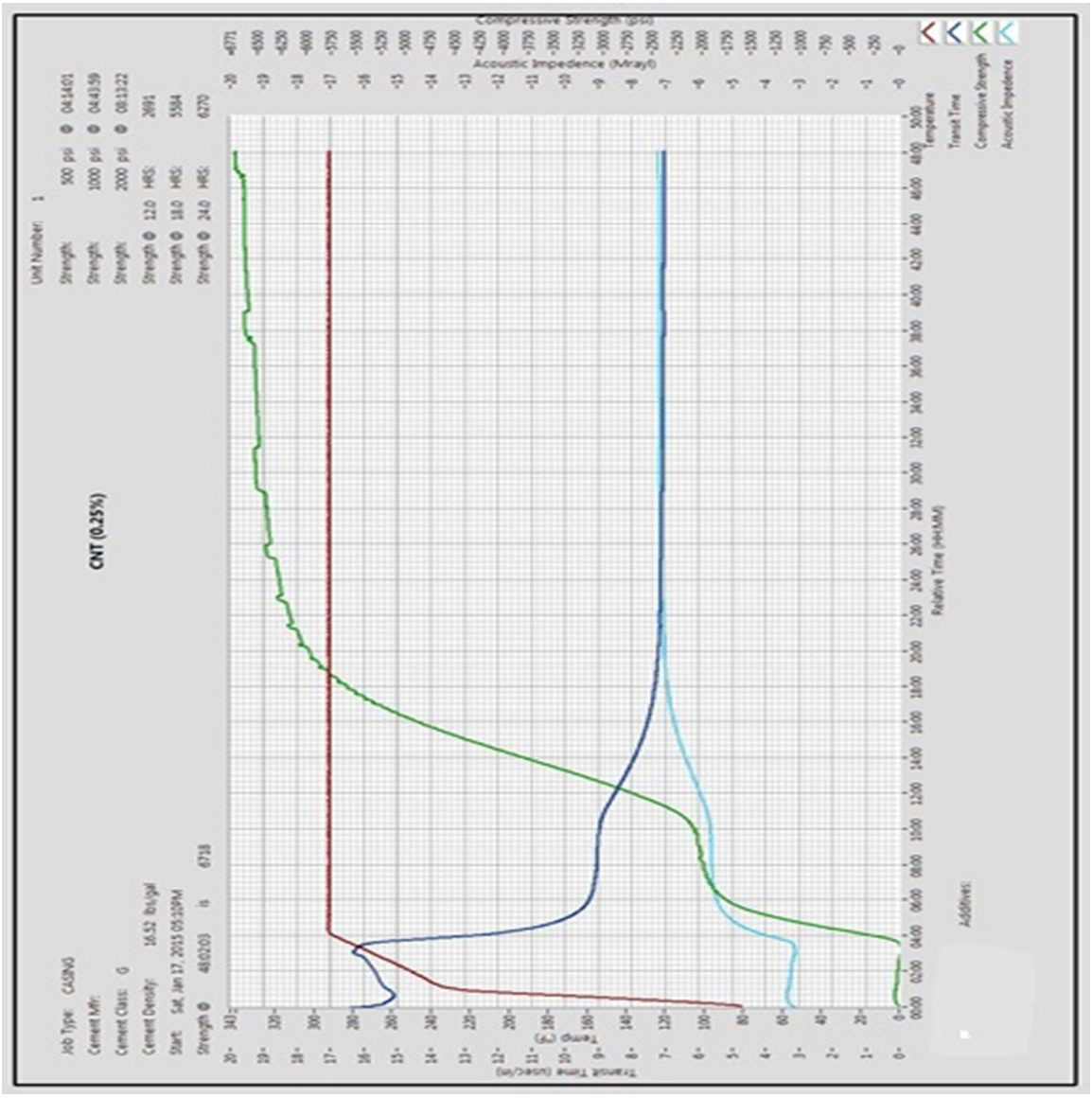

Figure 4.13: Compressive Strength development of 0.25% CNT cement slurry at HPHT

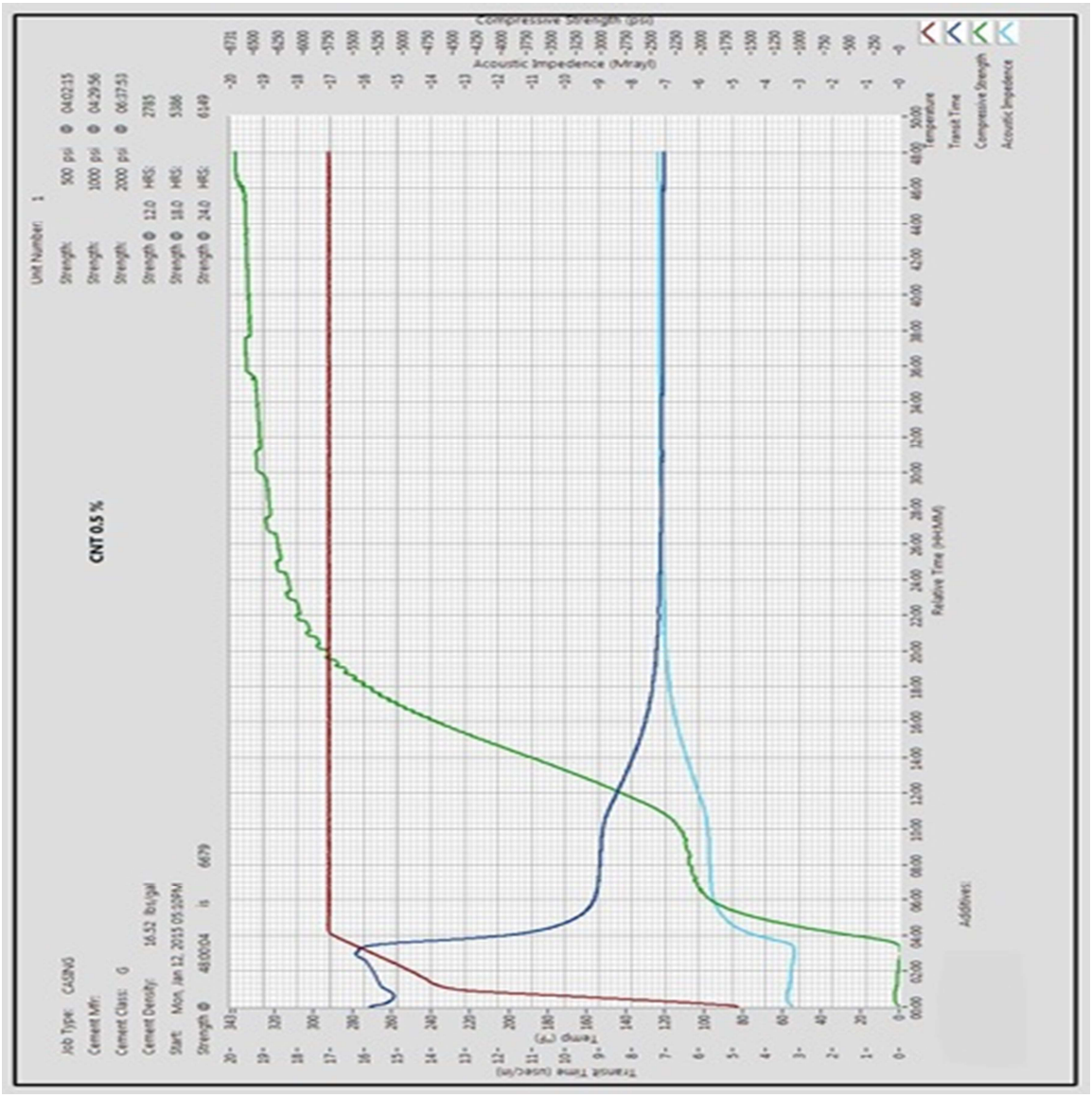

Figure 4.14: Compressive Strength development of 0.5% CNT cement slurry at HPHT

To solve this strength retrogression problem in selected well, 35% BWOC silica flour has been added to the cement design to get the base slurry for this particular well. Later, different CNT percentages are mixed in base slurry to study the mechanical potential of Carbon Nanotube as **Table** 4.3 explains the compressive strength tests results. It is evident that addition of CNT resulted in high early compressive strength as shown in **Figure** 4.12, **Figure** 4.13 and **Figure** 4.14. The 0.1% CNT cement system provides high compressive strength after 48 hours. The further addition resulted in low compressive strength.

Table 4.3: Compressive Strength results (Psi) at different time durations (12, 18, 24 & 48) hours

Time (HH : MM)	Class G	Base Mix	0.1% CNT	0.25% CNT	0.5%CNT
12:00	2487	2344	2953	2691	2785
18:00	2698	4965	5949	5584	5386
24:00	2744	5781	6893	6270	6149
48:00	-	6214	7274	6718	6679

Table 4.4: Time to gain Compressive Strengths (50, 500 & 2000 psi)

Compressive Strength (Psi)	Class G	Base Mix	0.1% CNT	0.25% CNT	0.5% CNT
	Time (HH : MM)				
50	01:25	03:33	03:33	03:34	03:45
500	01:58	04:00	03:57	04:14	04:21
2000	07:03	09:28	05:41	08:13	07:01

Table 4.4 represents the cement slurry development with time and focus on the time required for each cement system to develop a compressive strength of 50 Psi, 500 Psi and 2000 psi. These compressive strengths are considered sufficient enough to support the steel casing / liner prior to resuming the drilling operation. The transition period between developing a compressive strength of 50 psi and 500 psi is important and needed to be as short as possible to avoid long waiting time on cement before resuming drilling operation. Cement slurry of simple Class G cement has shortest time to attain the 500psi compressive strength as it gains the strength within 2 hours which shows its ability to set early. But Class G cement alone is not a good choice to inject in HPHT wells. The new cement system is designed according to selected well conditions as given in **Table** 3.1.

After performing the tests on cement systems containing different percentages of Carbon Nanotube, it is investigated that cement system having CNT percentage of (0.1% BWOC) yielded in the shortest transition period (24 minutes) of gaining compressive strength from 50 psi to 500 psi while the cement slurry having CNT percentage of (0%), (0.25%), & (0.5%) yielded on transition periods of (27, 30, & 31) minutes respectively with insignificant difference. (See **Figure** 4.15**).**

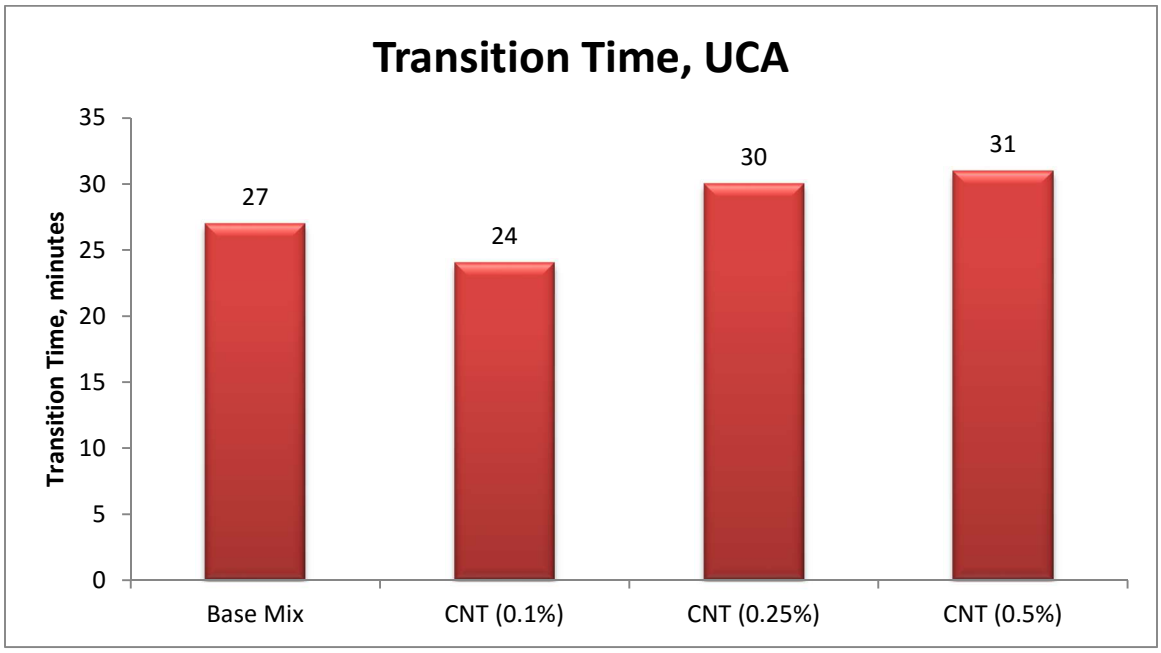

Figure 4.15: Transition time trend of achieving 50 to 500 psi compressive strength

Time to gain 2000psi compressive strength is important in case of perforations and stimulations. The 0.1% CNT cement system has the shortest time duration to gain 2000 psi compressive strength (see Figure 4.16). The 0.1% CNT cement system has the highest compressive strength after 48 hours.

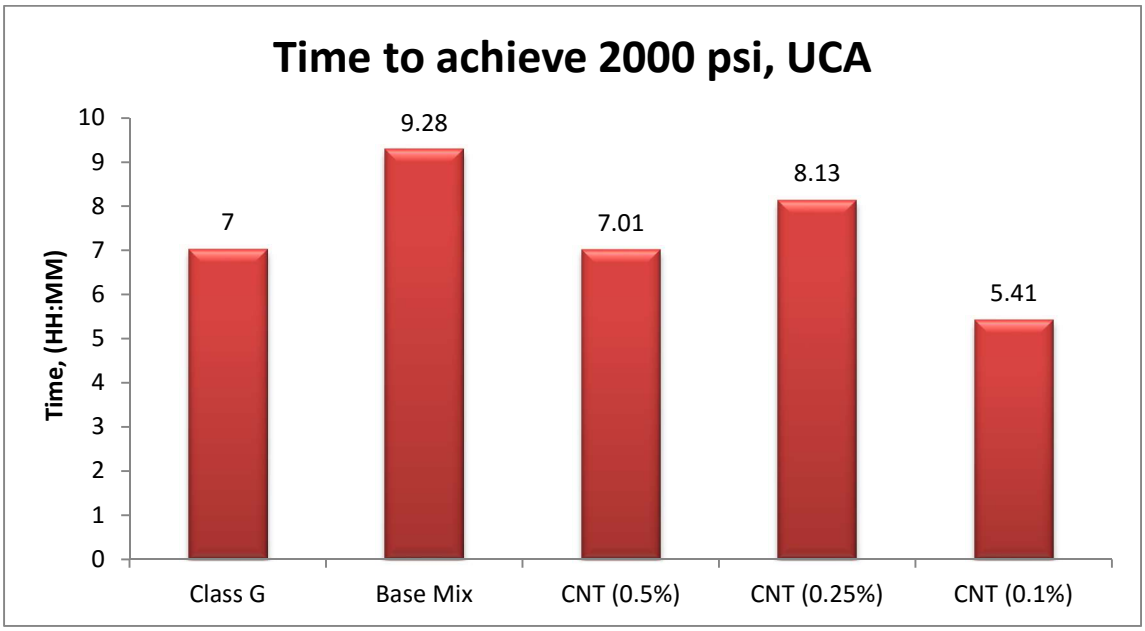

Figure 4.16: Time to gain 2000 psi Compressive Strength

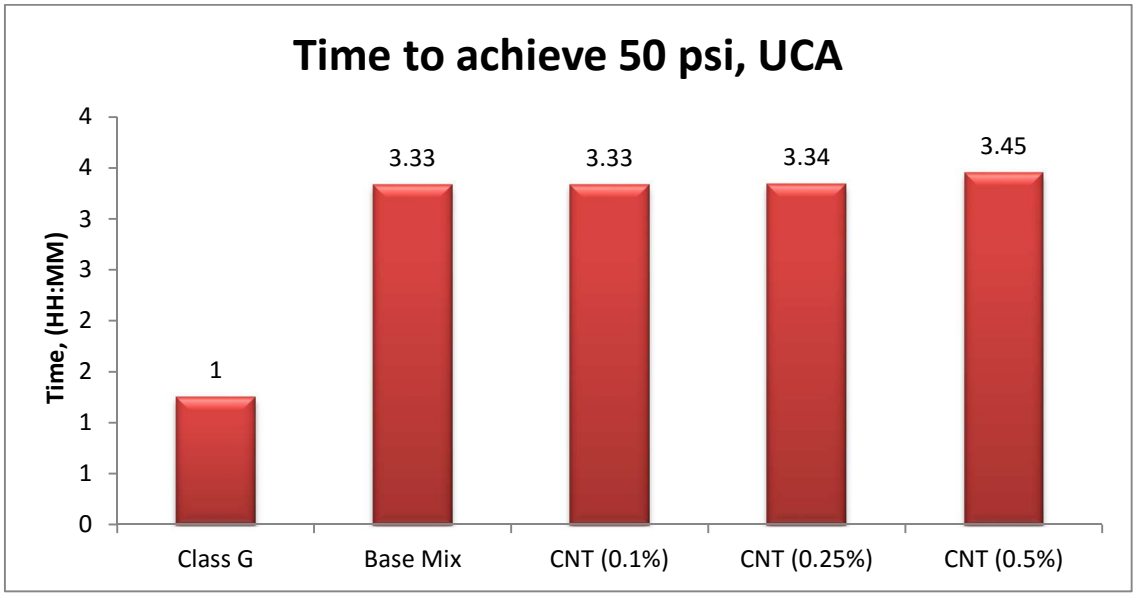

Figure 4.17: Time to gain 50 psi Compressive Strength

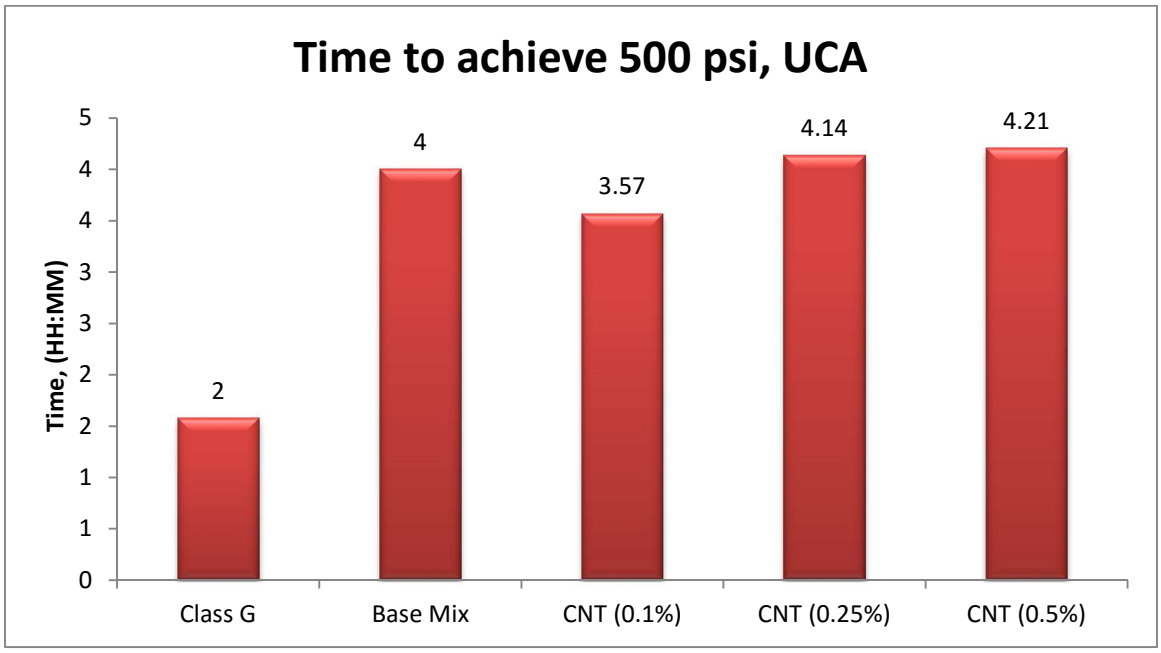

Figure 4.18: Time to gain 500 psi Compressive Strength

4.4.2 Effect of Carbon Nanotube on Destructive Compressive Strength

The four cement systems having Carbon Nanotubes percentages of (0 %, 0.1 %, 0.25 % and 0.5%) and class G cement have been subjected to the API compressive strength test in which the moulds of cement are made and cured at 290°F and 3000 psi pressure for 24 hours in HPHT curing machine. At the end of test, the cubes are removed from moulds and crushed to get compressive strength.

From **Figure** 4.19, it is obvious that cement system having 0.5% Carbon Nanotube BWOC has higher compressive strength as compared to other cement systems. It is found that addition of Carbon Nanotube by 0.5% BWOC increases the compressive strength. There is an increasing trend in the compressive strength of the cement system as the CNT

percentage is increased. 0.1% shows low compressive strength. This low compressive strength results as the consequence of low density.

The higher compressive strength is resulted from small size particles of CNT which acts as nano-filler and makes strong structure. Another reason was the high percentage availability of silica which provided more pozzolanic reaction which in result gave high compressive strength. The base mix was repeated with different WCR and observed that water contents affected the compressive strength as shown in Table 4.5. As the WCR is increased, it results in low compressive strength as compared to low WCR mix.

Later compressive strength test was conducted on different mixture mixed by different methods of mixing and concluded that the mixing process affected the compressive strength of cement. Dry mix, additives were blended in cement, has high compressive strength as compared to wet mix in which additives are mixed in water as obvious from the results.

Table 4.5: Effect of WCR on Compressive Strength

WCR %	Base Mix (Psi)
43.5	7463.6
44	5500

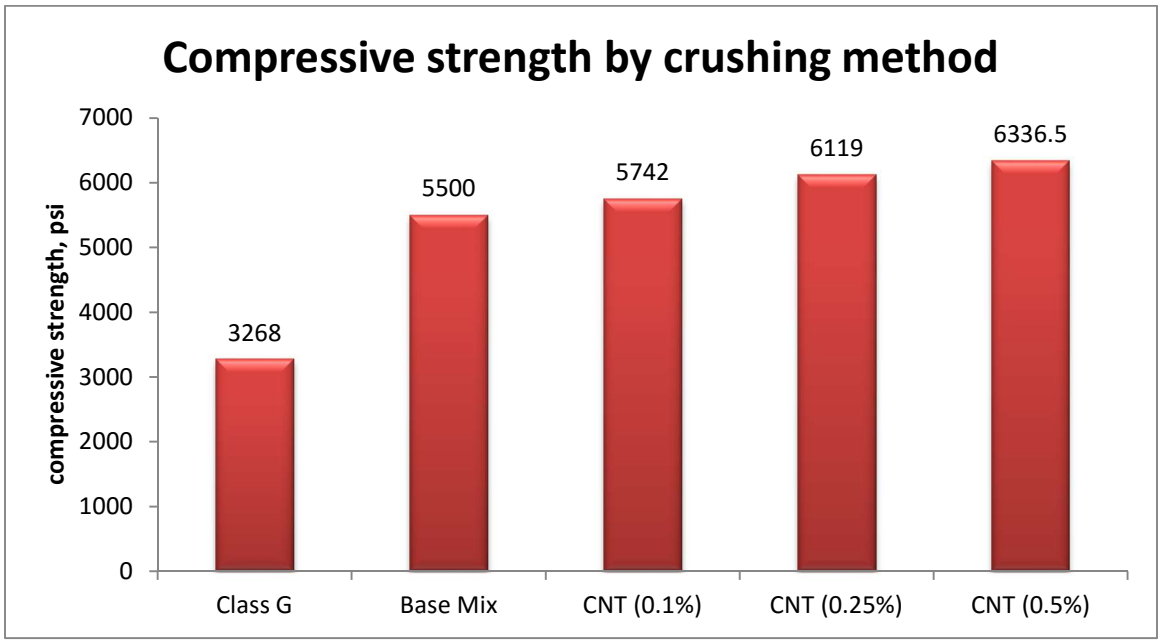

Figure 4.19: Compressive Strength trend by crushing method

4.5 EFFECT OF CARBON NANOTUBE ON POROSITY AND PERMEABILITY

Permeability determines the ability of fluid to flow at different pressure and helps in determining the long term performance of cement. As the cement sheath is supposed to seal the zones and prevents fluid migration. This is only possible if we have low permeability.

In this test, cement plugs have been drilled out of cubes of cement and conducted the permeability and porosity tests on the automated porosimeter/permeameter at 500psi confining pressure.

Table 4.6 explains CNT effects on the permeability and porosity of cement after curing at 24 hours. In new formulated slurries, the CNT mix makes non uniform particle distribution which results in reduction of porosity and permeability of slurries. When simple class G cement is subjected to high temperature and pressure conditions, it results in high porosity and permeability results. This behavior of Class G causes low integrity and high gas migration problem. Later cement slurry designed without CNT was subjected to such extreme conditions and it resulted in low permeability and porosity. The addition of CNT by 0.5% BWOC results in reduction in the permeability. There is a very little change in the permeability of cement as the percentage of CNT is decreased to 0.25% and 0.1% compare to 0.5% CNT (see **Figure** 4.20). As already mentioned that decreasing the CNT percentage, decreases the density; thus permeability decreases.

Porosity shows a decreasing trend as the percentage of CNT is increased. 0.5 % CNT has the lowest porosity and as the percentage is decreased, there is a rise in the porosity (see **Figure** 4.21).

Table 4.6: Porosity and permeability of CNT (0.1%, 0.25% & 0.5%) cement systems after 24 hours of curing

Parameters	G Class	Base Mix	0.1% CNT	0.25% CNT	0.5% CNT
Permeability (md)	0.358	0.0041	0.0001	0.0001	0.0001
Porosity (%)	36	31	30	27	26

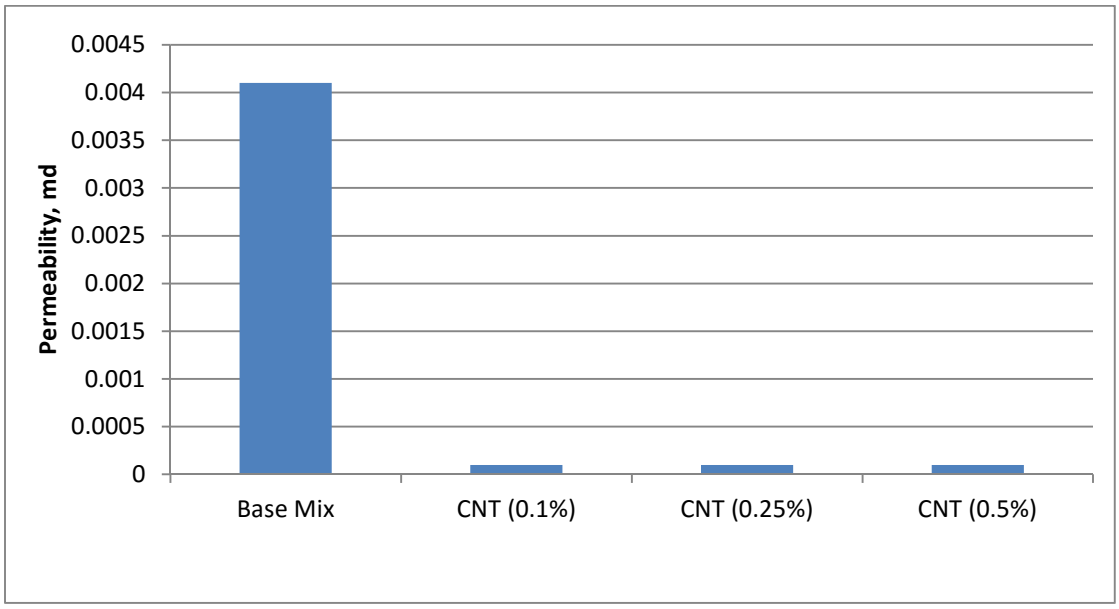

Figure 4.20: Permeability trend of CNT admixed slurries

Figure 4.21: Porosity trend of CNT admixed slurries

4.6 EFFECT OF CARBON NANOTUBE ON RHEOLOGY

The rheological properties of an oil well cement (OWC) slurry defines the quality of the final product and assists predicting its end use performance and physical properties during and after processing. Rheological measurements can determine the flow properties of the cement slurry such as plastic viscosity, yield point, gel strength, etc. Rheology studies the flow of fluids and deformation of solids under stress and strain.

Table 4.7 presents the rheological results of different CNT percentages (0%, 0.1%, 0.25% &0.5%) BWOC with simple class G. It is evident from the results that simple G class cement slurry has low rheological properties that it cannot improve the mud displacement in these particular well conditions. The cement system has been designed for a particular well depending on its condition (see **Table** 3.2). Different kinds of additives are incorporated in Class G cement to improve its rheological properties. Later, CNT is incorporated in different percentages to base slurry and subjected to rheology test. It is observed that addition of CNT to the base slurry caused improvement in rheological properties (PV and YP). **Figure** 4.22 and **Figure** 4.23 show the trends of rheological properties changes. It should be noted that increase in CNT percentage results in thicken of cement slurry. It is obvious that the addition of CNT to base cement system results in rise of plastic viscosity of cement. As the plastic viscosity is a function of solid particles so the addition of CNT to cement increases the solid particles which in turn enhance the viscosity. Also, the increase in plastic viscosity of the cement will help keep the solid particles in suspension of the cement. This helps in efficient displacement of mud by the

cement. The change in yield point is not much even up to the addition of 0.5% CNT (see **Figure** 4.23). This shows that as the CNT percentage is increased, the yield point is increased but there is no significant change in it. It is always desirable for the cement slurry to have low yield points.

Table 4.7: Rheology of CNT admixed cement slurries at HPHT

Properties	**Class G**	**Base Mix**	**0.1% CNT**	**0.25% CNT**	**0.5% CNT**
Plastic Viscosity (cp)	32.24	131.14	278	277	276
Yield Point $lb_f/100ft^2$	16.4	9.65	6	8	11

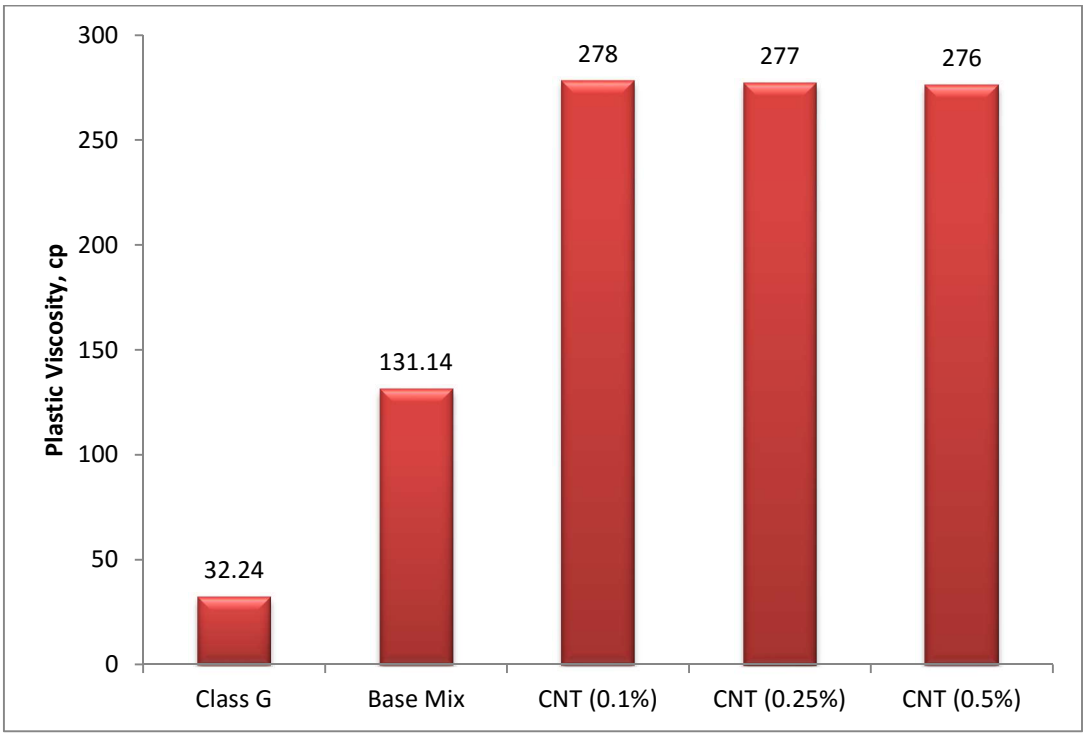

Figure 4.22: Plastic Viscosity variation for different concentrations of CNT

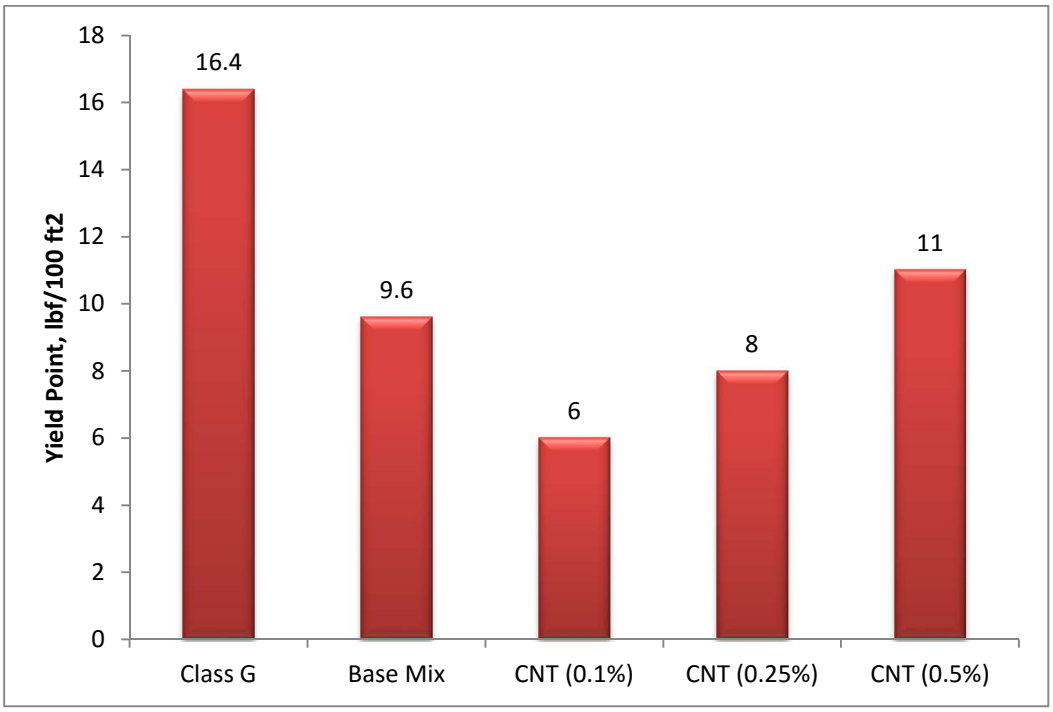

Figure 4.23: Yield Point variation for different concentrations of CNT

It is evident from **Figure** 4.22 that oil well cement incorporating MWCNT will have high viscosities. This will help the cement in efficient mud displacement which is also an important factor in successful oil well cementing. Later, all cement systems are subjected to gel strength tests which is measure of the attractive forces in particles that cause the development of gelation when flow is stopped. It also explains the force required to initiate the flow after stopping circulation. Gel strength test is conducted on Fann Viscometer and results are provided in **Table** 4.8. It is evident from the results that the addition of CNT in base cement results in change in gel strength. The CNT addition does not put prominent effects on the initial gel strength, 10- sec, as the results are almost same in all CNT cement systems. Actually the addition of CNT decreases the initial gel

strength as compared to base mix. When the CNT cement systems are subjected to 10-min gel strength, they affect the gelling behavior of cement slurries. It is evident from the results that for all the CNT cement systems the 10-min gel strength results are higher as compared to base mix. There is an increasing trend in the 10-min gel strength as the CNT percentage is increased. (see **Figure** 4.24).

Table 4.8: Gel Strengths result of G class, (0,0.1,0.25,0.5)% CNT admixed slurries

Gel Strength $lb_f/100ft^2$	**Class G**	**Base Mix**	**0.1% CNT**	**0.25% CNT**	**0.5% CNT**
10-sec	7	9	4	5	5
10-min	20	27	37	38	40

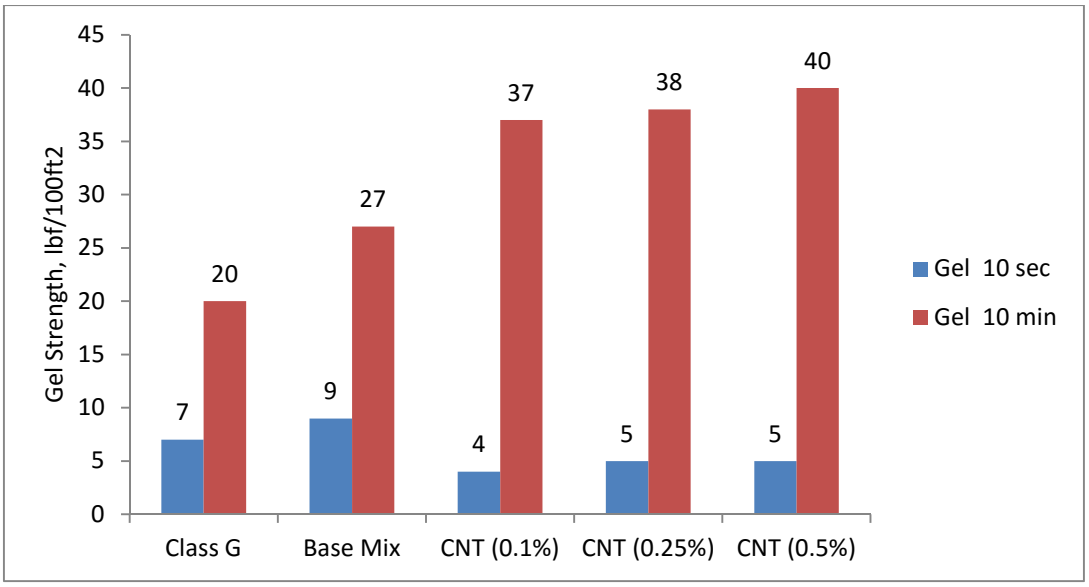

Figure 4.24: Effect of CNT on gel strength

4.7 MICROSTRUCTURAL ANALYSIS

The microstructure of cement slurry is studied using both SEM and XRD analysis. SEM explains the composition and pore structure. While XRD is well-known techniques for studying cement composition and hydration. The hydration products of Class G oil well cement mainly depend on the curing temperature. The results indicated that the major hydration products of clean cement slurry are calcium silicate hydrate gel CSH (II) [Ca2SiO4·3H2O], C2SH2[Ca2SiO4·2H2O], C3S2H3· [Ca3(HSiO4)2·2H2O], calcium hydroxide CH[Ca(OH)2], ettringite Aft [3CaO·Al2O3·3CaSO4·32H2O] and monosulphate Afm [3CaO·Al2O3·CaSO4·12H2O]. The XRD patterns of neat class G cement slurry hardening paste under low and higher temperatures are given **Figure 4.26** and **Figure 4.27** respectively.

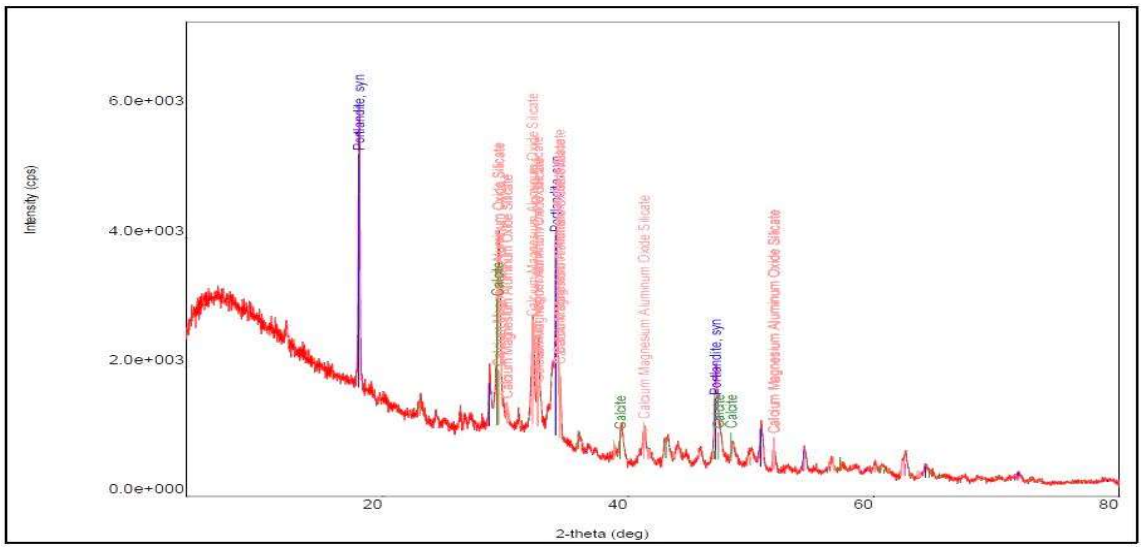

Figure 4.25: XRD spectra of G type cement after 8 hours hydration at ambient condition

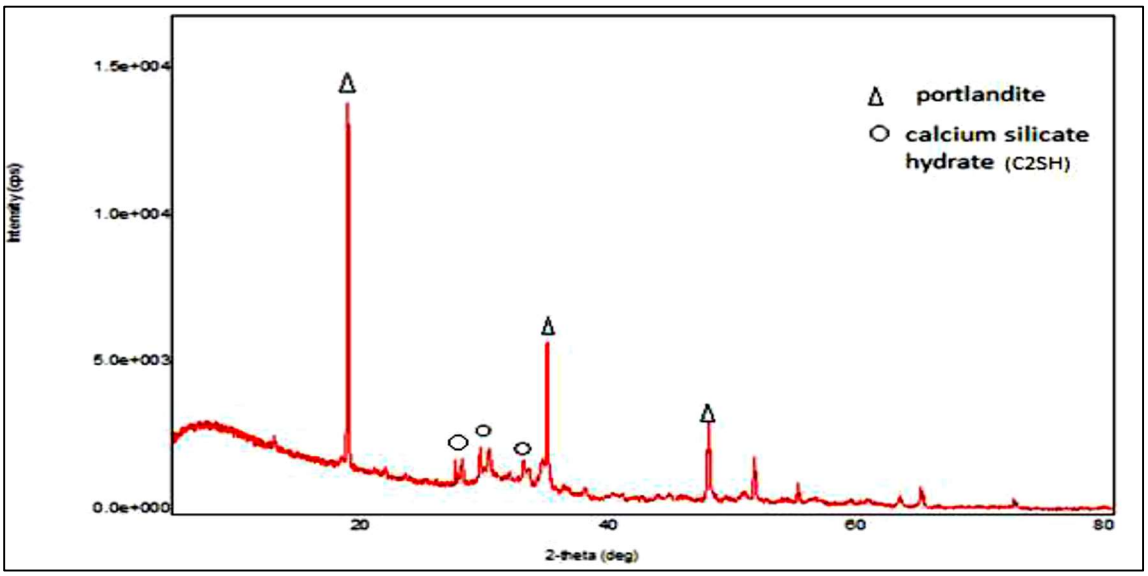

Figure 4.26: XRD spectra of G type cement after 24 hours hydration at HPHT condition

It is evident that hydration of cement at low temperature leads to formation of portlandite (CH) and calcium silicate hydrate (CSH) which is not detected at low temperature hydration because of amorphous behavior at low conditions.

When the curing temperature exceeded 110 °C, the products CSH (Ⅱ) began to be transformed into C2SH [$Ca_2SiO_4 \cdot H_2O$] called α-dicalcium silicate hydrate. Under these conditions, there was no difference between the product compositions for different temperatures, but the amount of each product could vary with curing temperature because there were slight differences in the peak intensity for the XRD pattern of different curing temperatures. With the increase of curing temperature, di-poly-silicate hydration products

began to increase. The analysis given above indicates that the major products of Class G oil well cement were CH and CSH (Ⅱ) when curing at low temperature conditions.

CSH (Ⅱ) is a fiber-shaped, in which the fiber can branch at every 0.5 μm length during the growth of the particle. The branches of these particles adhere to each other and form a continuous three-dimensional network in the hardened paste. Thus, when the curing temperature is below 110 °C, the major hydration products mentioned above could adhere to each other to give the hardened paste with obvious characteristics of a network structure. But when the curing temperature exceeded 110 °C, with the products being transformed into the high crystallinity product C_2SH, which is in the shape of a plate-block, the microstructure of the hardened paste was also transformed from a fiber network into the morphology of a pile of plate-blocks. Since C_2SH is a very weak and porous matter, and the bonding stress between these big block crystals is weak, the structural stress of hardened paste would partially concentrate and increase, the compressive strength would decrease to some extent. With the increase of curing temperature, the crystalline grain of C_2SH became much larger, and many mass blocks were piled up in the hardened paste.

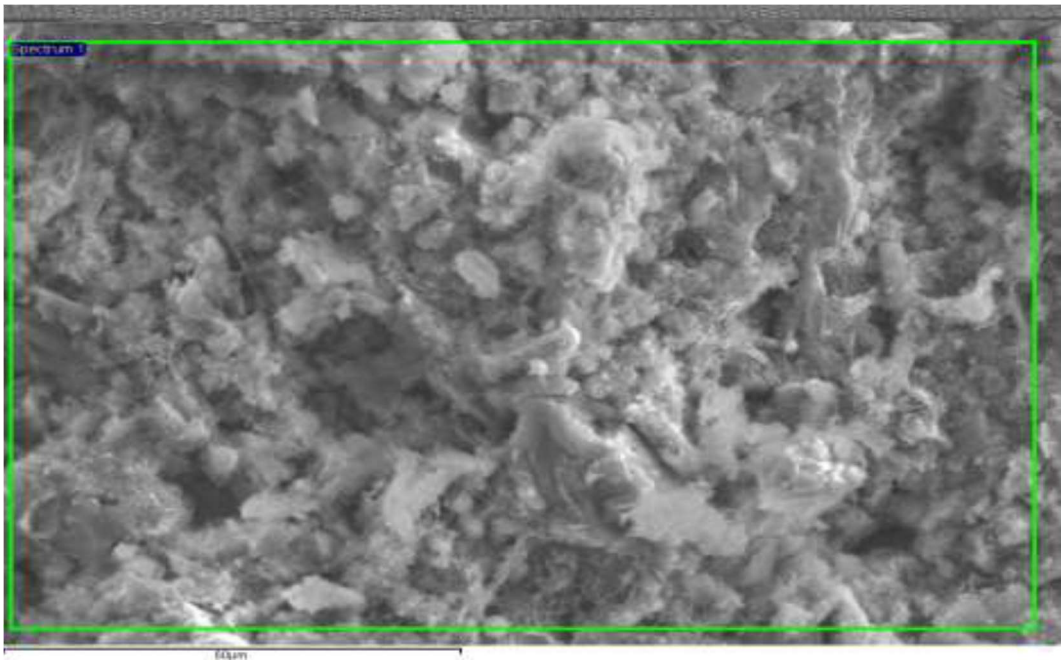

Figure 4.27: SEM of hydration products of simple class G cement cured at normal conditions for 8 hours.

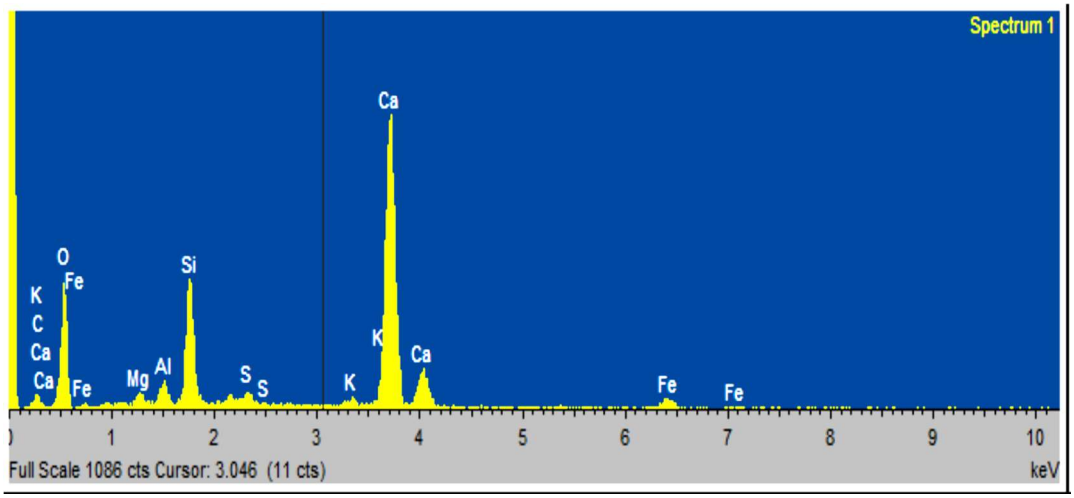

Figure 4.28: EDX of hydration products of simple class G cement cured at normal conditions for 8 hours

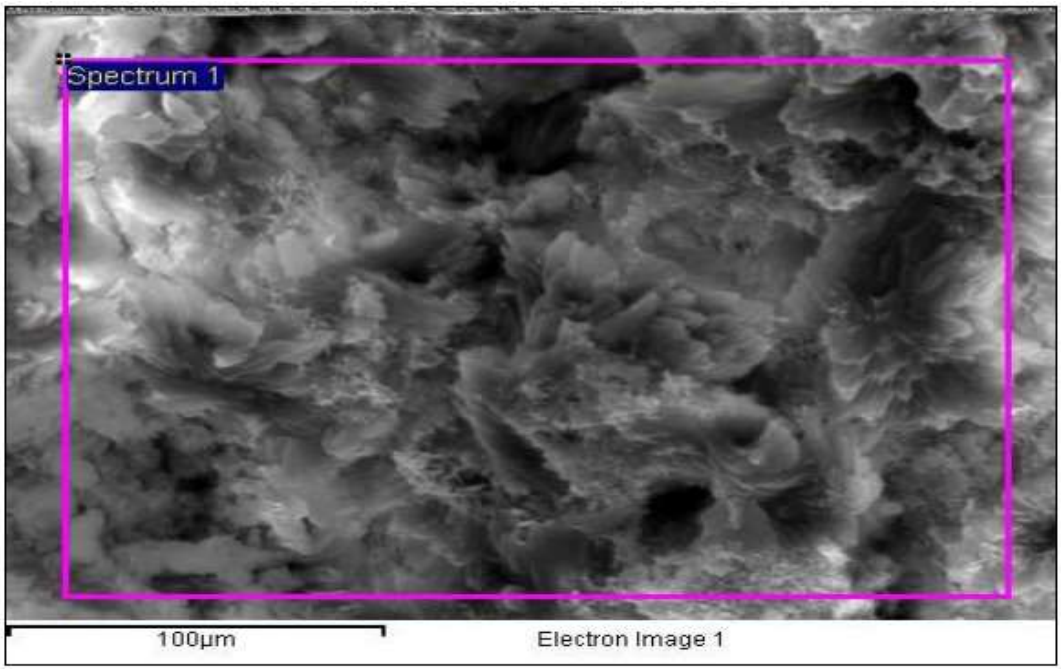

Figure 4.29: SEM of hydration products of simple class G cement cured at high conditions (144°C) for 24 hours

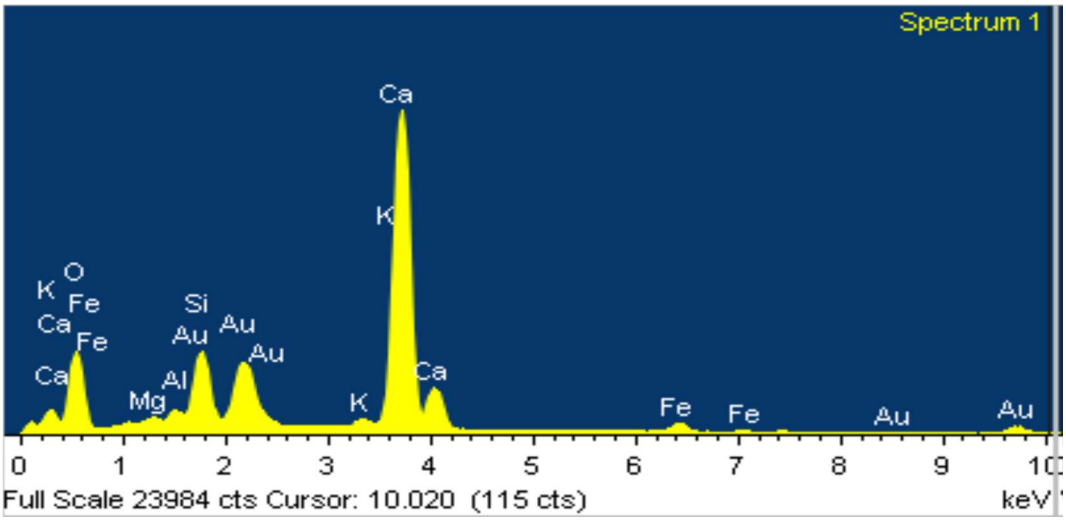

Figure 4.30: EDX of hydration products of simple class G cement cured at HPHT for 24 hours

When 35% BWOC of silica flour was added to the cement slurry, the hydration products were totally different from clean slurry under the curing condition of 144 ℃, 3000 psi and 1 day. There were obvious specific peaks of SiO_2 in the XRD patterns. But the specific peaks of CH weakened with the increase of the amount of silica flour. The specific peaks of CH and C_2SH almost disappeared in the hydration products when 35% silica flour was added to the cement slurry. This indicates that a great amount of C_2SH had been transformed into $C_5S_6H_5$ (tobormorite). Under this condition, there still were specific peaks of SiO_2 in the XRD pattern (see **Figure** 4.31).

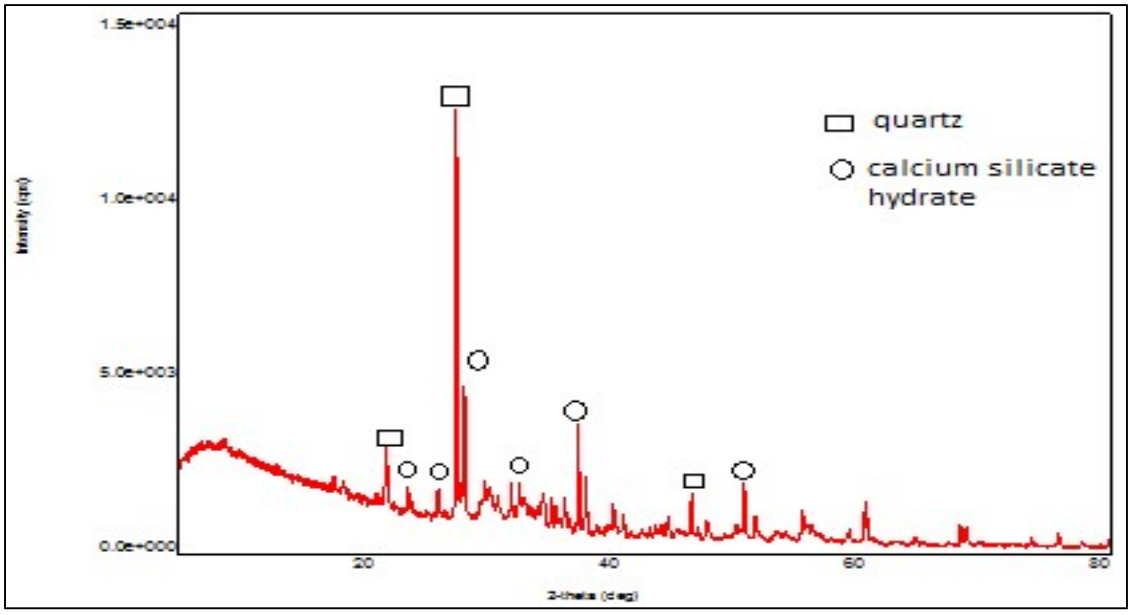

Figure 4.31: XRD spectra of hydration products containing 0% CNT cured at HPHT conditions for 24 hours

In cement slurry with silica flour, $C_5S_6H_5$ could be produced during hydration and it was a kind of good crystal with needle shape. These needle shape of $C_5S_6H_5$ products could interweave and join each other to build an ideal and well-proportioned network structure in hardened paste (see **Figure 4.33**). So set cement could retain a high compressive strength.

Even from the EDX (**Figure 4.34**) it is evident that CSH percentage is quite high after the hydration of cement cured at HPHT conditions.

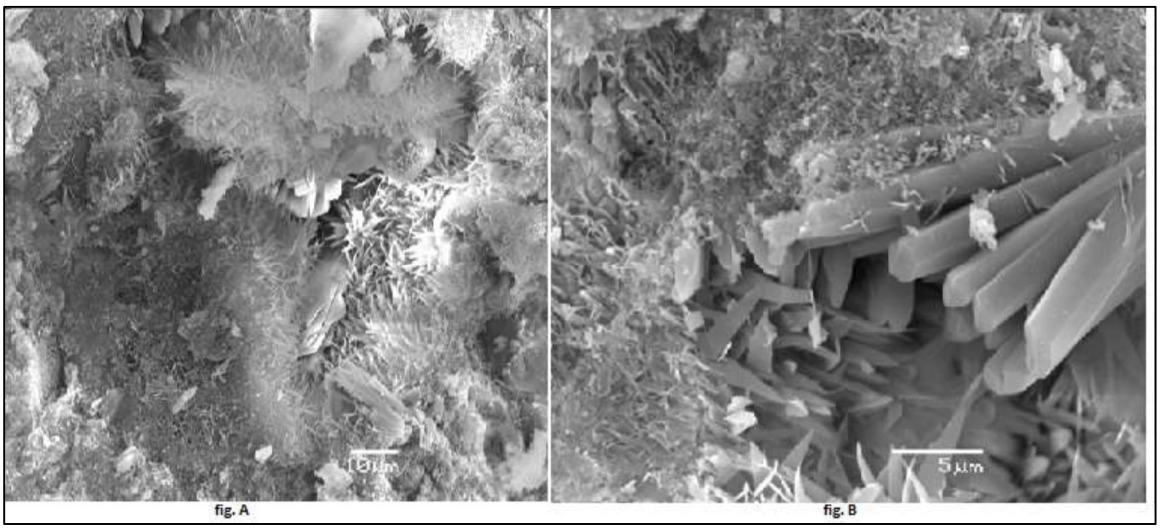

Figure 4.32: SEM photographs of hydration products of 0% CNT cement slurry cured at HPHT conditions for 24 hours.

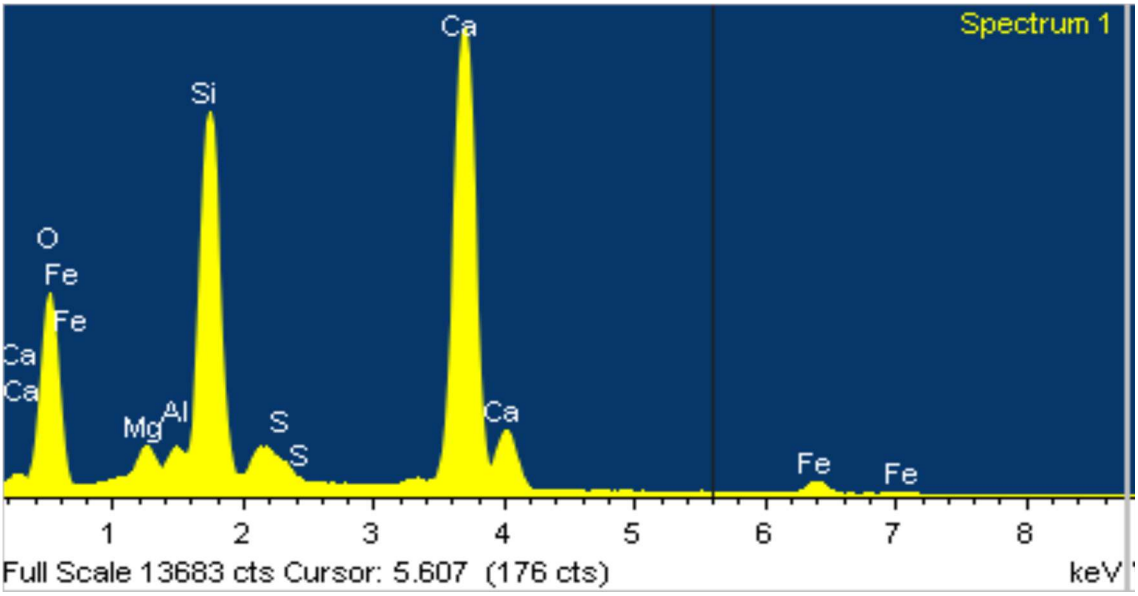

Figure 4.33: EDX of hydration products of 0% CNT cement slurry cured at HPHT conditions for 24 hours

As the CNT was incorporated in the mix, it formed more polymerization and least CH appeared in the mix. The smaller particle size and greater surface area reacted with CH in solution to produce more CSH. Less CH was available for diffraction.

In cement slurry with CNT, highly dense CSH is produced, and it was a kind of good crystal that provides high compressive strength. These crystal products could interweave and join each other to build an ideal and well-proportioned network structure in hardened paste (see **Figure** 4.35 & **Figure** 4.36). The small size of CNT helps in filling the capillaries and resulted in dense structure. So set cement could retain a high compressive strength. CNT acts as a nano-filler in the cement matrix which also is a reason for high compressive strength of cement.

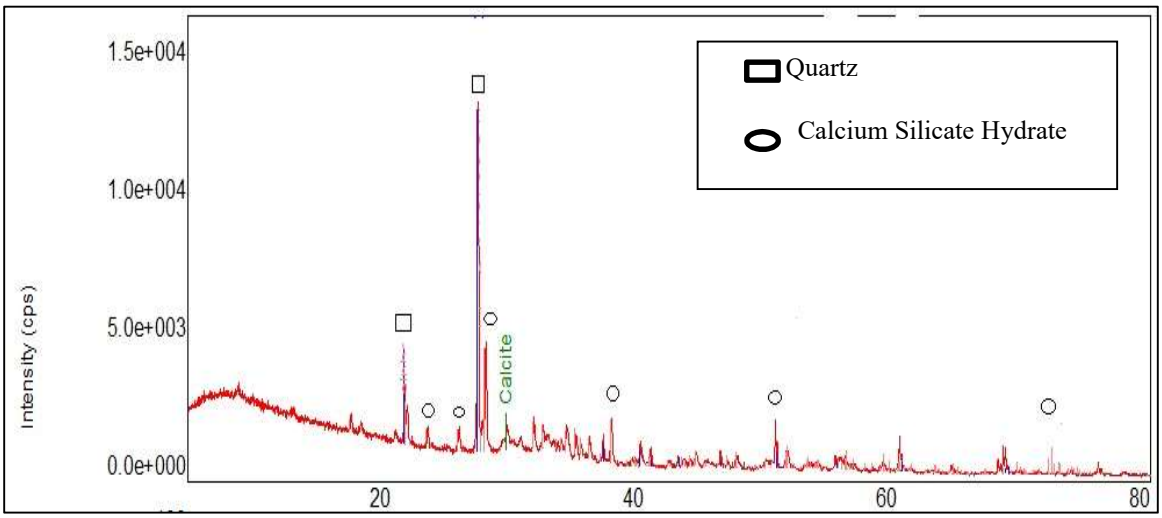

Figure 4.34: XRD of hydration products of 0.1% CNT cement slurry cured at HPHT conditions for 24 hours

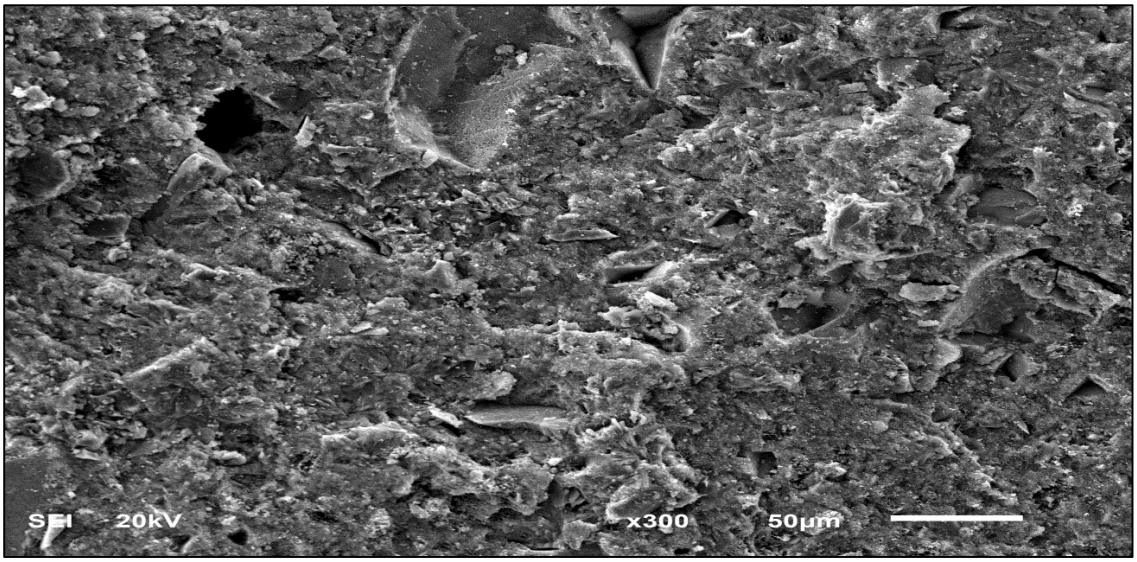

Figure 4.35: SEM image of hydration products of 0.1% CNT cement slurry cured at HPHT conditions for 24 hours.

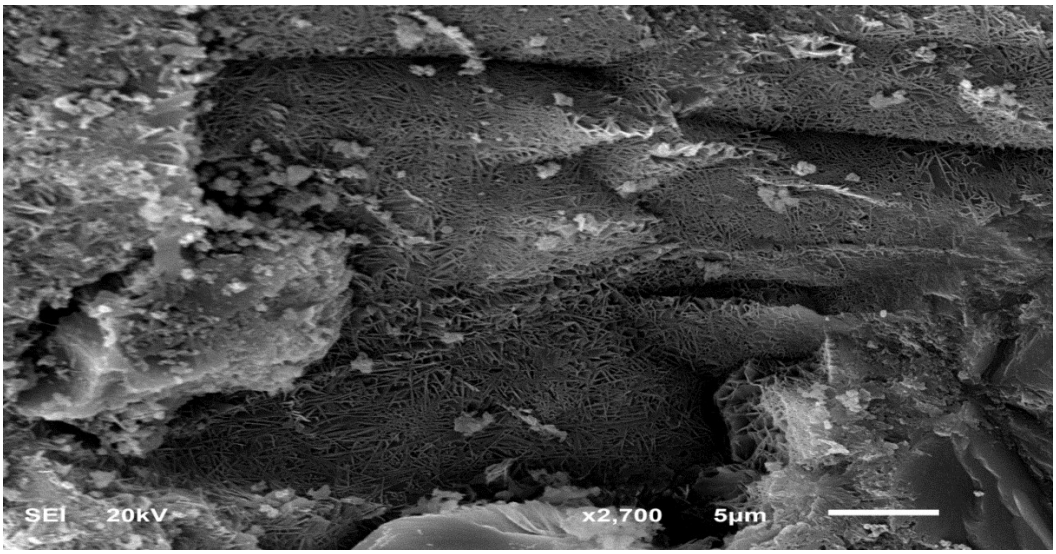

Figure 4.36: SEM image of hydration products of 0.1% CNT cement slurry cured at HPHT conditions for 24 hours.

During the hydration of cement slurry with CNT by 0.25%, high percent of quartz (SiO_2) could be produced during hydration with CSH. These crystals of SiO_2 products could interweave and join each other to build an ideal and well-proportioned network structure in hardened paste (**Figure 4.39**).

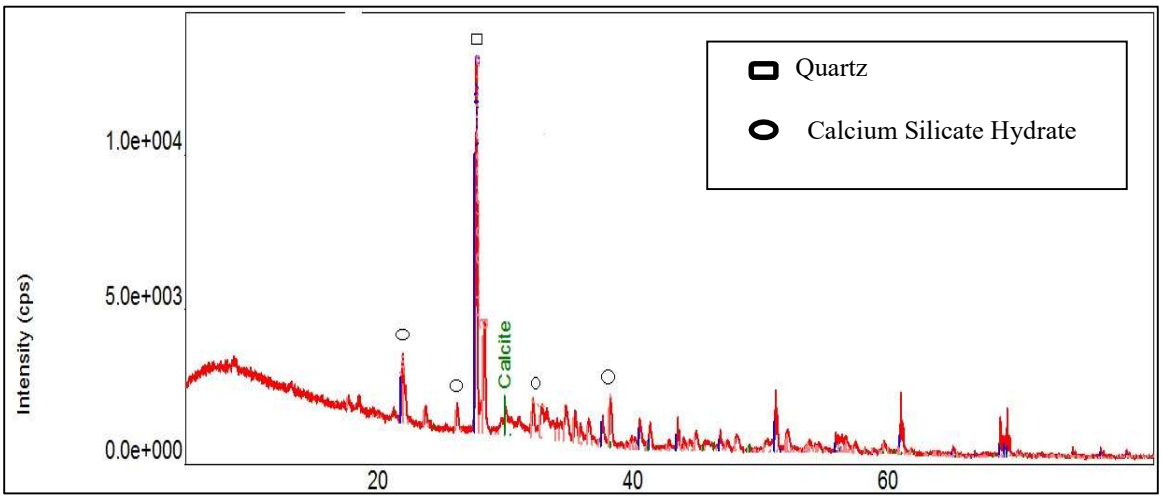

Figure 4.37: XRD of hydration products of 0.25% CNT cement slurry cured at HPHT conditions for 24 hours

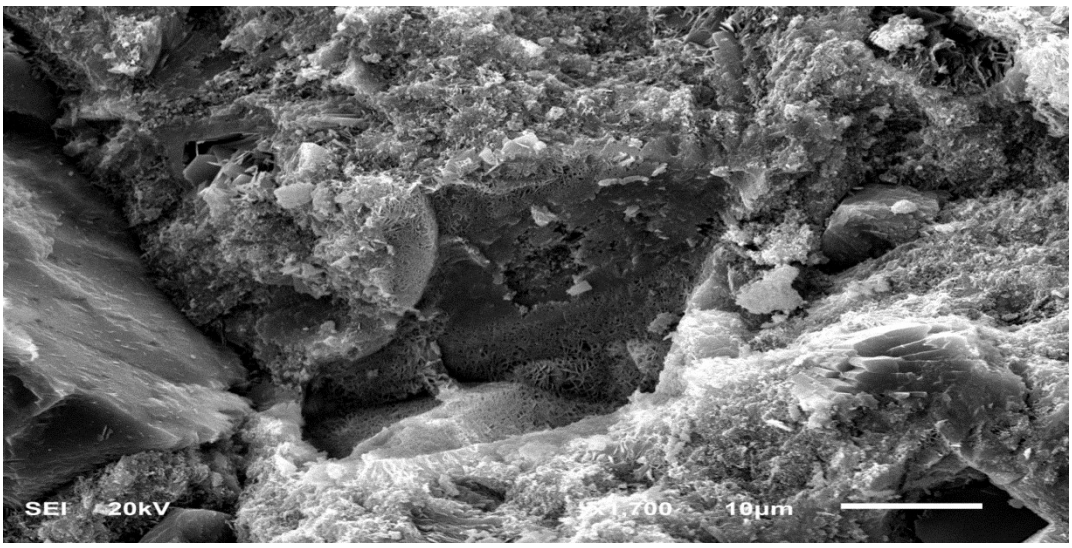

Figure 4.38: SEM image of hydration products of 0.25% CNT cement slurry cured at HPHT conditions for 24 hours.

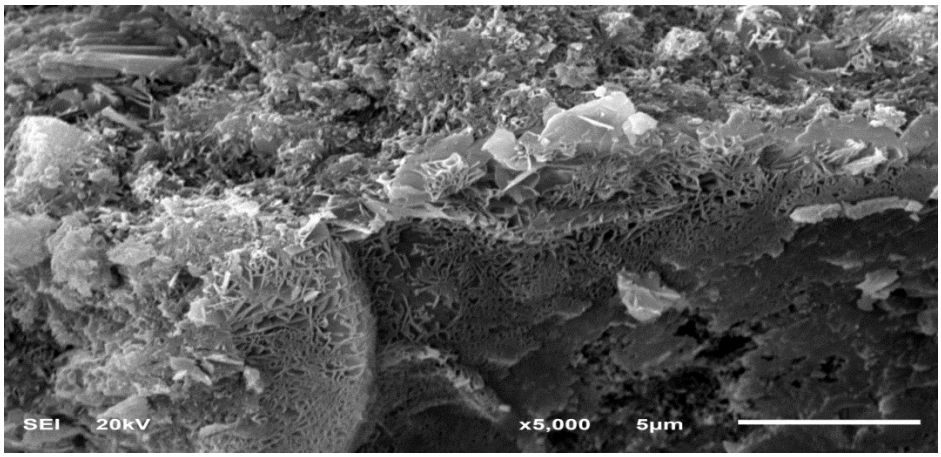

Figure 4.39: SEM image of hydration products of 0.25% CNT cement slurry cured at HPHT conditions for 24 hours.

As the CNT was added by 0.5% BWOC in cement slurry, it produced a more dense structure and helped in more pozzolanic reaction which contributed in higher compressive strength. From SEM analysis, it can be observed that more crystals are formed with 0.5% CNT in cement.

Figure 4.40: SEM image of hydration products of 0.5% CNT cement slurry cured at HPHT conditions for 24 hours.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

This thesis is directed to assess the effect of CNT on Portland Saudi cement type 'G' in high pressure and temperature cementing applications. Tests required to characterize the performance of cement with CNT have been conducted under HPHT conditions. Thickening time, free water separation, slurry density, rheological properties, compressive strengths, fluid loss and porosity and permeability tests have been conducted. The results of this study are restricted to the selected well conditions, cement used, chemical additives, percentages of CNT, and cement slurry preparation and testing procedures. This study would be useful for researchers interested in this area and would provide valuable information for the enhancement of state of the art CNT in cement.

5.1 CONCLUSIONS

The findings of this investigation highlight the importance of CNT in cement design. Conclusions made from the research are summarized as follows;

1) From thickening time test, it is observed that CNT acts as an accelerator as it increases the hydration reaction. So it might not be helpful in deep well cementing.

2) There is no free water separation in all CNT cement systems after aging as CNT acts as a nano-filler and blocks the capillaries and prevents the water flow.
3) The addition of lower percentage of CNT reduces the density of cement slurries. But 0.5% CNT increases the density of cement slurry. But the difference in density is minimal.
4) It is investigated that CNT addition increases the viscosity and yield point of cement slurry. This behavior makes the CNT viscosifier which helps in mud displacement.
5) From the compressive strength by sonic method, it was investigated that addition of CNT by 0.1% BWOC resulted in high early compressive strength. The further addition in CNT percentage resulted in low compressive strength.
6) From the compressive strength by destructive method, it was investigated that addition of CNT by 0.5% BWOC resulted in high early compressive strength. The further reduction in CNT percentage resulted in low compressive strength.
7) From the permeability and porosity investigations, it can be concluded that CNT addition decreases permeability and porosity. In conventional design, the particles are distributed uniformly but in this particular design with CNT, the particles distribution is non-uniform. So, they resulted in low permeability and porosity. Permeability was very low for all the CNT percentages and 0.5% CNT resulted in low porosity.

8) From the microstructural analysis, it is obvious that small particles of CNT fill the pores and block the capillaries in the cement. In result, they provide the dense cement structure.
9) SEM images show that CNT acts as a nano-filler in the cement matrix.

5.2 RECOMMENDATIONS

This work includes the findings of CNT effects on oil-well cement properties in high pressure and temperature applications but still a lot of work left to be done. The impact of CNT effects in shallow applications with low pressure and temperature should also be investigated.

CNT effects can also be investigated with different water to cement ratios. Also the impact of other Nano materials including Nano alumina, Nano clay, Nano silica and Nano zeolite should be investigated. Different combinations of different nano material can be used for further investigation on HPHT cement applications.

LIST OF ABBREVIATIONS

μ_p	Plastic Viscosity
API	American Petroleum Institute
ASTM	American Standards for Testing and Measurement
Bc	Bearden Consistency Unit
BHCT	Bottomhole Circulating Temperature
BHP	Bottomhole Pressure
BHST	Bottomhole Static Temperature
BWOC	By Weight of Cement
BWOW	By Weight of Water
HPHT	High Pressure High Temperature
HSR	High Sulphate Resistant
ISO	International Organization for Standardization
MSR	Moderate Sulphate Resistant
MW	Mud Weight
CNT	Carbon Nanotube
OSR	Ordinary Sulphate Resistant
OWC	Oil Well Cement
PCF	Pound per Cubic Feet
PV	Plastic Viscosity
RPM	Rotation per Minute
SEM	Scanning Electron Microscope
TRB	Time to Reach Bottom
TVD	Total Vertical Depth
UCA	Ultrasonic Cement Analyzer
WOC	Wait on Cement
XRD	X-ray Diffraction
YP	Yield Point

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